Supporting Information

Substrate-Controlled Rh(II)-Catalyzed Single-Electron-Transfer (SET): Divergent Synthesis of Fused Indoles

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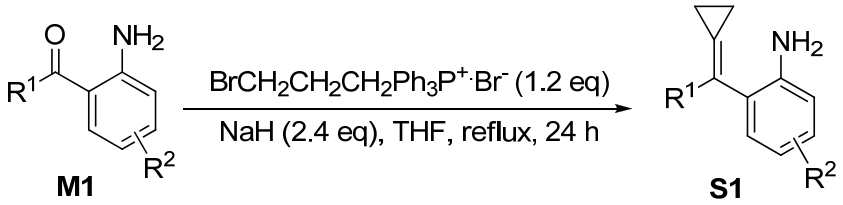
General remarks

Dichloromethane was freshly distilled from calcium hydride; THF, Et_2O and toluene were distilled from sodium (Na) under argon (Ar) atmosphere. Melting points were determined on a digital melting point apparatus and temperatures were uncorrected. ^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker AM-300 or AM-400 spectrophotometers. Infrared spectra were recorded on a Perkin-Elmer PE-983 spectrometer with absorption in cm-1. Flash column chromatography was performed using 300-400 mesh silica gel. For thin-layer chromatography (TLC), silica gel plates (Huanghai GF254) were used. Mass spectra were recorded by EI, and HRMS were measured on a HP-5989 instrument.

General procedure for the synthesis of MCPs

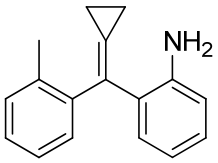


Compounds **M1** were prepared according to the previous literature.[1]

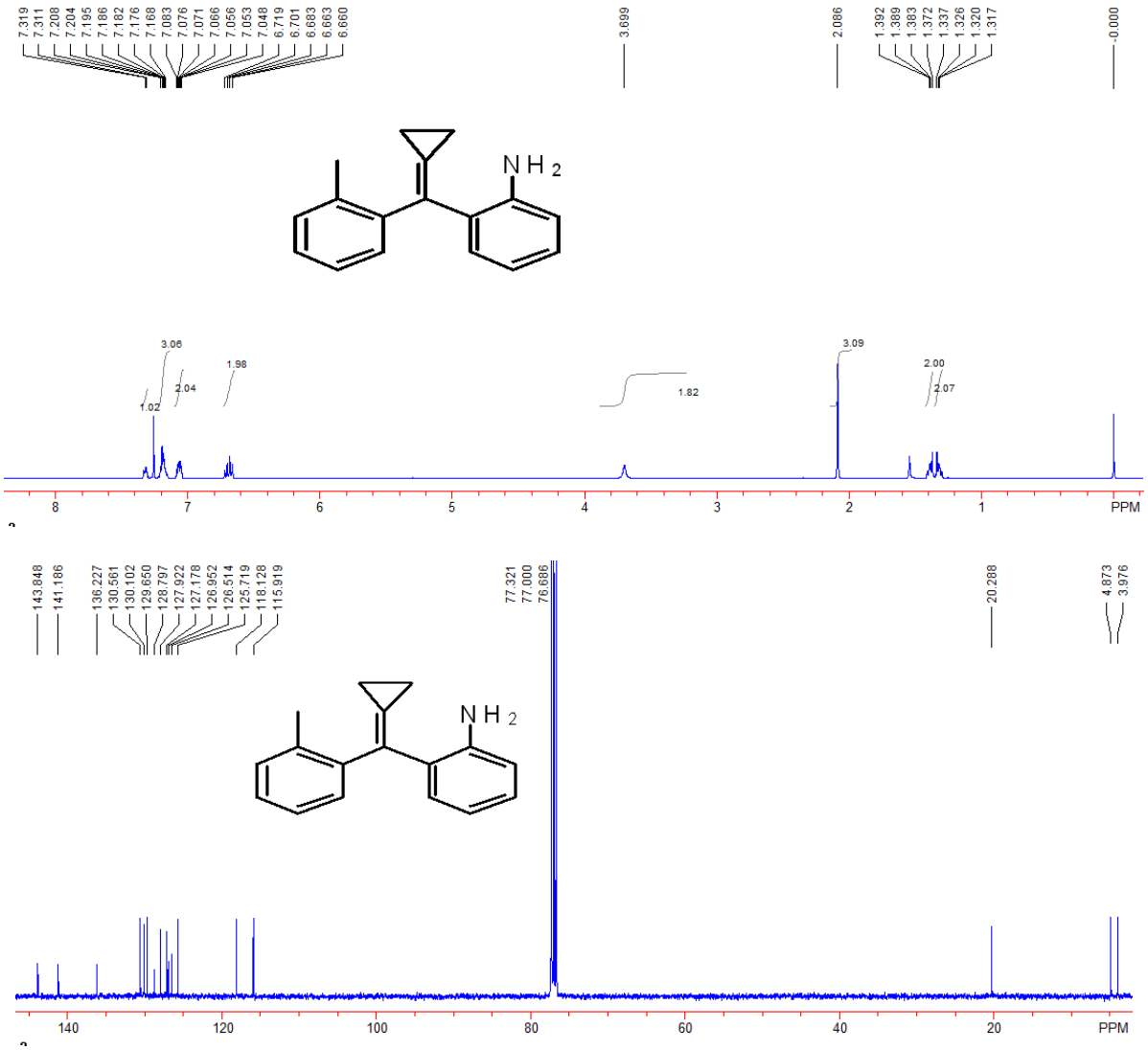
A solution of 3-bromopropyltriphenylphosphonium bromide (5.5 g, 12 mmol) and NaH (576 mg, 24 mmol) in THF (10 mL) was stirred at 70 ^{o}C for 12 h. Afterwards **M1** (10 mmol) in THF (5 mL) was added and the reaction solution was stirred at 70 ^{o}C for another 12 h. Then the solvent was removed under reduced pressure and the residue was purified by silica gel flash chromatography (eluent: petroleum ether / ethyl acetate = 50/1) to afford the products in moderate yields.[2]

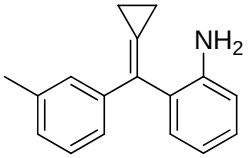
Other MCPs were prepared according to our previous work.[3]

Spectroscopic data for compounds S1b, S1c, S1g and S1i

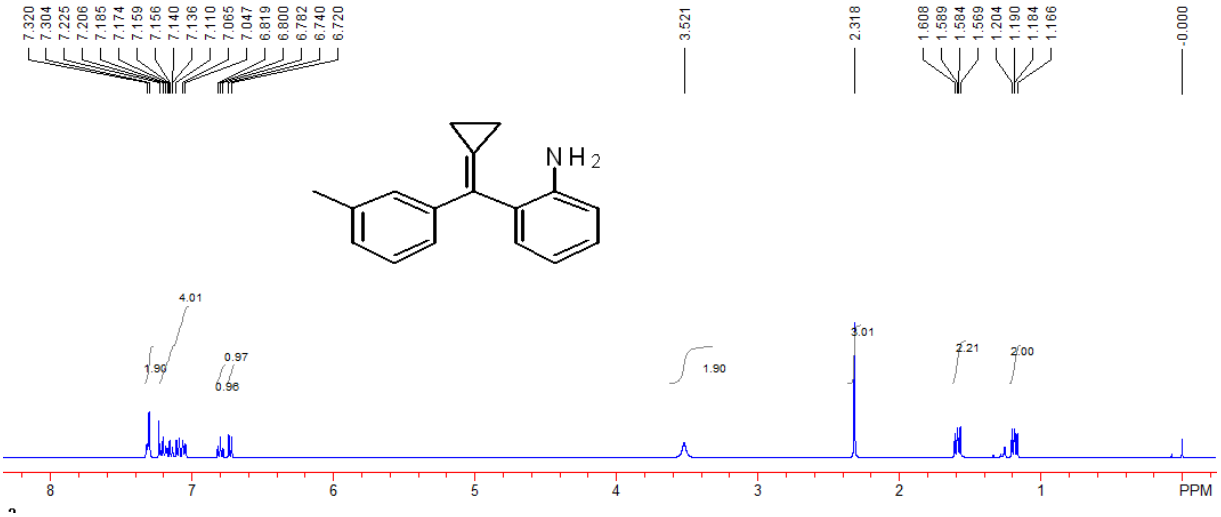


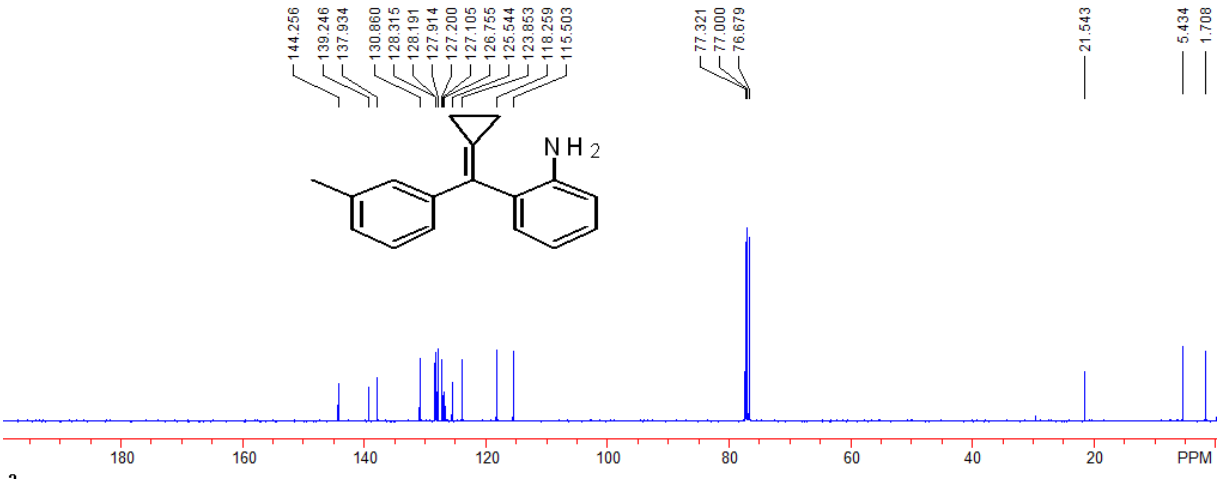
Compound S1b: 940 mg, 40%, A yellow solid, m.p. 76-78 ^{o}C; IR (CH_2Cl_2): ν 3471, 3022, 2978, 1612, 1513, 1452, 1303, 750 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 1.32-1.34 (m, 2H), 1.37-1.39 (m, 2H), 2.09 (s, 3H), 3.70 (s, 2H), 6.66-6.72 (m, 2H), 7.05-7.08 (m, 2H), 7.17-7.21 (m, 3H), 7.31-7.32 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 4.0, 4.9, 20.3, 115.9, 118.1, 125.7, 126.5, 127.0, 127.2, 127.9, 128.8, 129.7, 130.1, 130.6, 136.2, 141.2, 143.8; MS (ESI) *m/z*: 236.1 ($M+H^+$, 100); HRMS (ESI) Calcd. for $C_{17}H_{18}N^+$ requires: 236.1434, found: 236.1432.

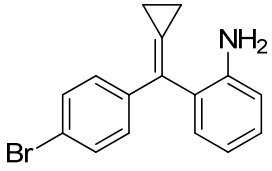




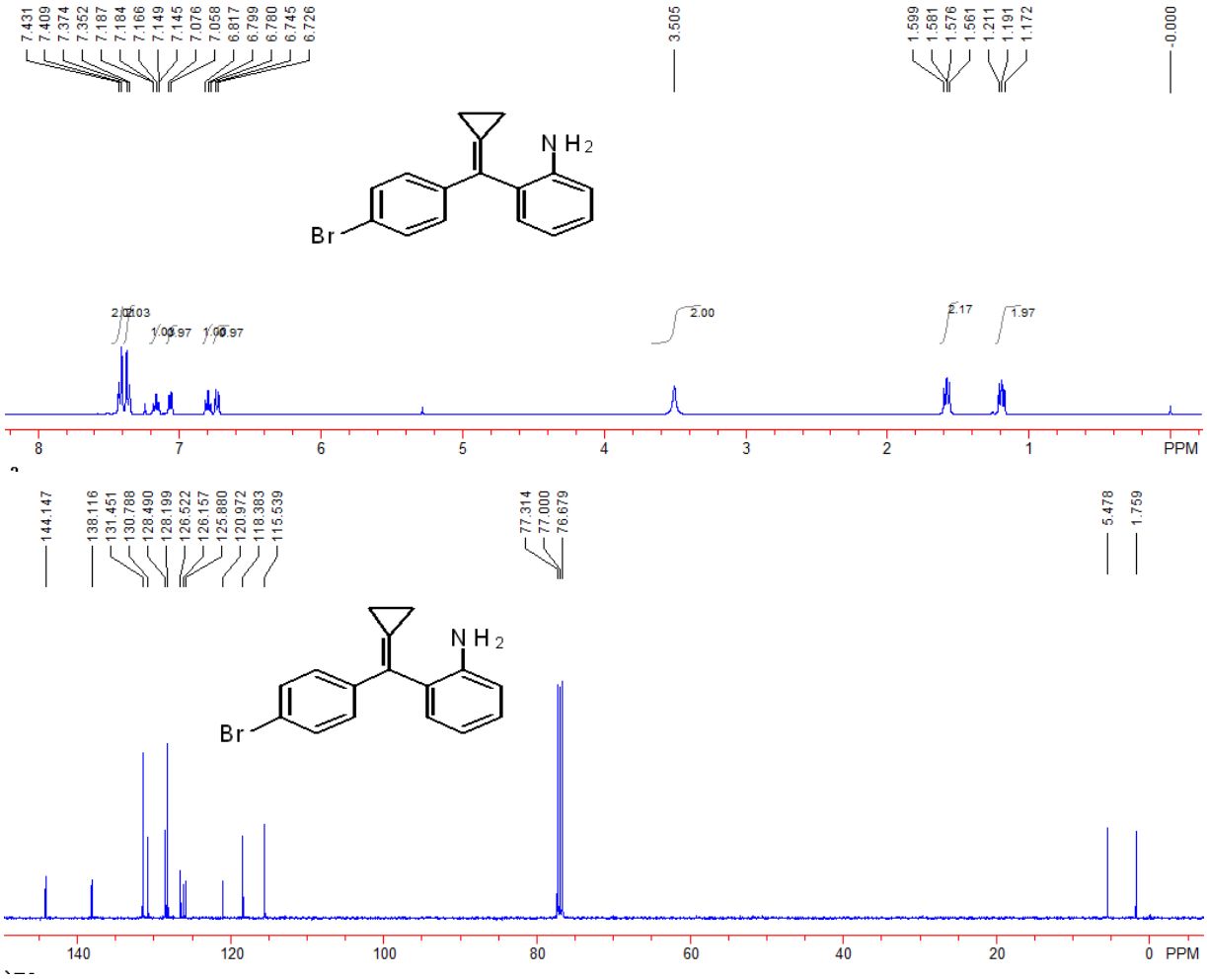
Compound S1c: 940 mg, 40%, A yellow solid, m.p. 80-82 ^{o}C; IR (CH_2Cl_2): ν 3472, 3381, 3018, 2972, 1611, 1492, 1451, 1303, 746 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 1.17-1.20 (m, 2H), 1.57-1.61 (m, 2H), 2.32 (s, 3H), 3.52 (s, 2H), 6.73 (d, J = 8.0 Hz, 1H), 6.80 (dd, $J_1 = J_2$ = 7.6 Hz, 1H), 7.05-7.23 (m, 4H), 7.30-7.32 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 1.7, 5.4, 21.5, 115.5, 118.3, 123.9, 125.5, 126.8, 127.1, 127.2, 127.9, 128.2, 128.3, 130.9, 137.9, 139.2, 144.3; MS (ESI) *m/z*: 236.1 ($M+H^+$, 100); HRMS (ESI) Calcd. for $C_{17}H_{18}N^+$ requires: 236.1434, found: 236.1437.

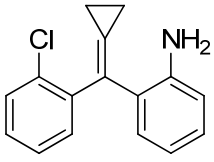






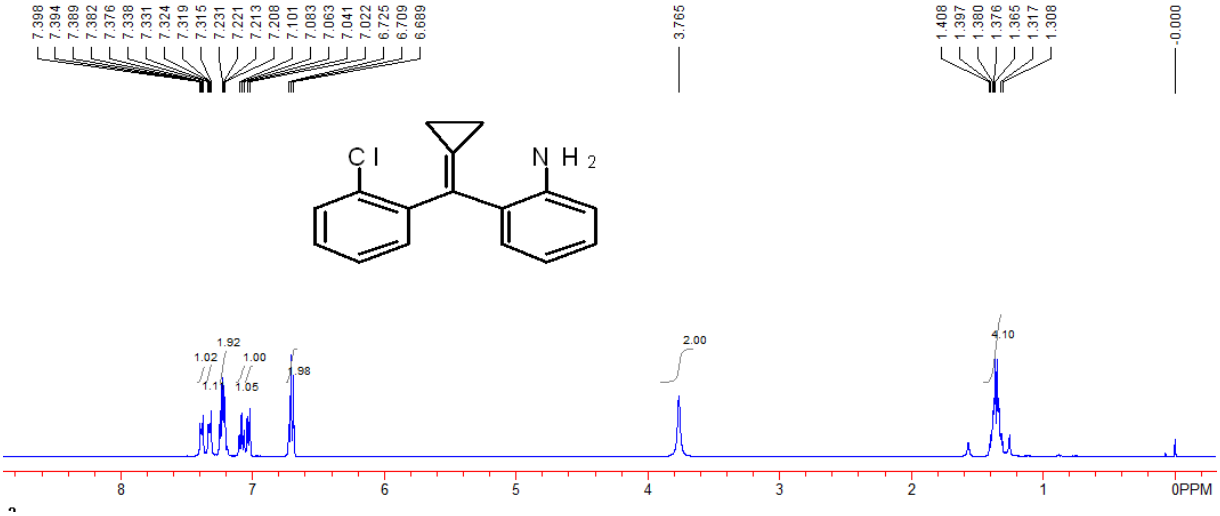
Compound S1g: 1.47 g, 49%, A yellow solid, m.p. 130-132 ^{o}C; IR (CH_2Cl_2): ν 3470, 3377, 3027, 2971, 1618, 1484, 1007, 903, 749 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 1.17-1.21 (m, 2H), 1.56-1.60 (m, 2H), 3.51 (s, 2H), 6.74 (d, J = 7.6 Hz, 1H), 6.80 (dd, $J_1 = J_2$ = 7.6 Hz, 1H), 7.07 (d, J = 7.2 Hz, 1H), 7.15-7.19 (m, 1H), 7.36 (d, J = 8.8 Hz, 2H), 7.42 (d, J = 8.8 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 1.8, 5.5, 115.5, 118.4, 121.0, 125.9, 126.2, 126.5, 128.2, 128.5, 130.8, 131.5, 138.1, 144.1; MS (ESI) *m/z*: 300.0 (M+H$^+$, 100); HRMS (ESI) Calcd. for $C_{16}H_{15}BrN^+$ requires: 300.0382, found: 300.0388.

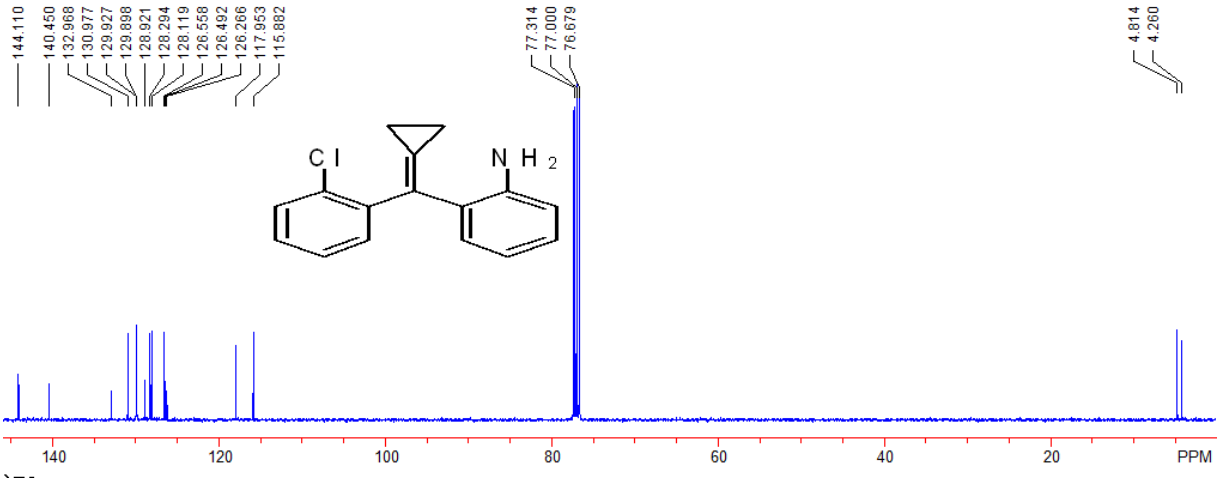




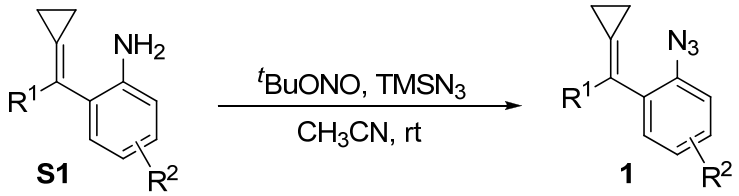
Compound S1i: 998 mg, 39%, A yellow solid, m.p. 82-84 ^{o}C; IR (CH_2Cl_2): ν 3470, 3380, 3052, 2974, 1612, 1493, 1034, 906, 748 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 1.31-1.41 (m, 4H), 3.77 (s, 2H), 6.69-6.73 (m, 2H), 7.03 (d, J = 7.6 Hz, 1H), 7.06-7.10 (m, 1H), 7.21-7.23 (m, 2H), 7.32-7.34 (m, 1H), 7.38-7.40 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 4.3, 4.8, 115.9,

118.0, 126.3, 126.5, 126.6, 128.1, 128.3, 128.9, 129.90, 129.93, 131.0, 133.0, 140.5, 144.1; MS (ESI) *m/z*: 256.1 ($M+H^+$, 100); HRMS (ESI) Calcd. for $C_{16}H_{15}ClN^+$ requires: 256.0888, found: 256.0892.



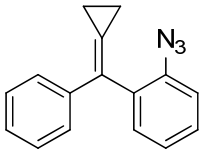


General procedure for the synthesis of compounds 1

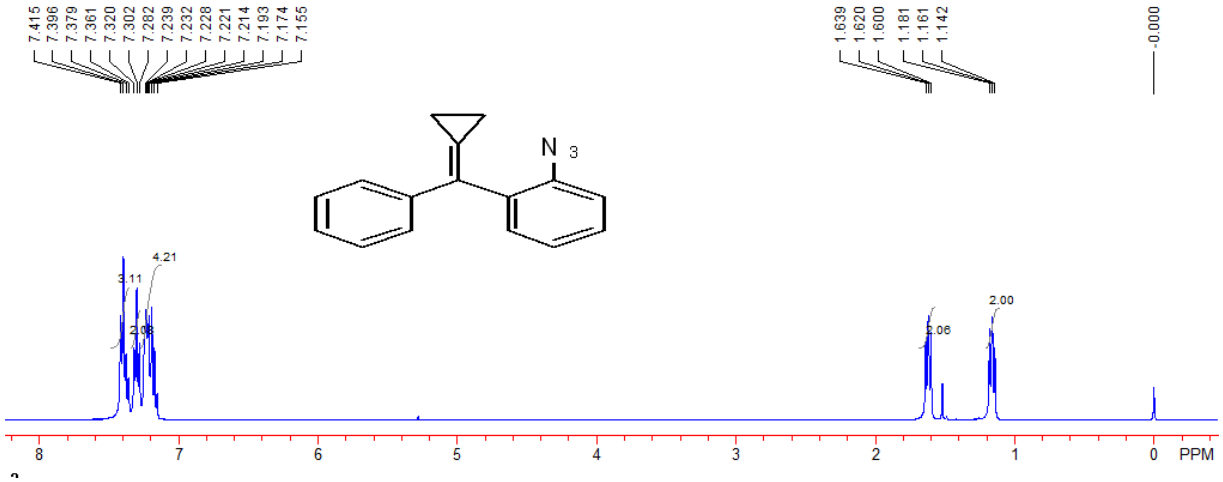


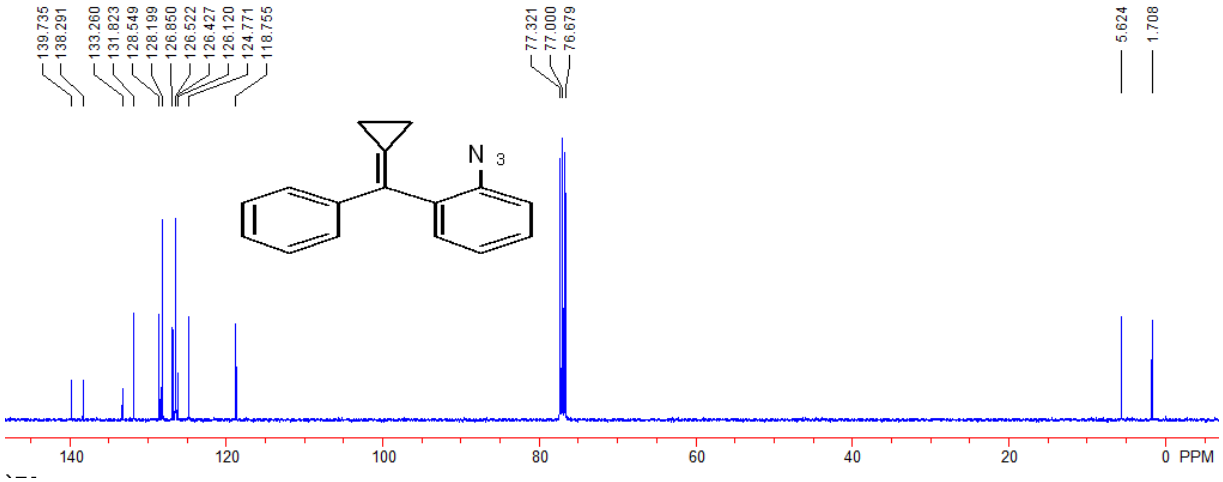
To a solution of **S1** (1 mmol) in CH_3CN (5 mL) were added ^tBuONO (178 μL, 1.5 mmol) and $TMSN_3$ (262 μL, 2 mmol), then the resulting reaction mixture was stirred at room temperature for 4 h. The solvent was removed under reduced pressure and the residue was purified by silica gel flash chromatography (eluent: petroleum ether / ethyl acetate = 50 / 1) to afford the product in moderate yield.

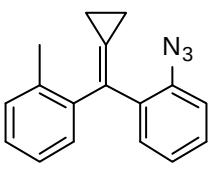
Spectroscopic data for compounds 1



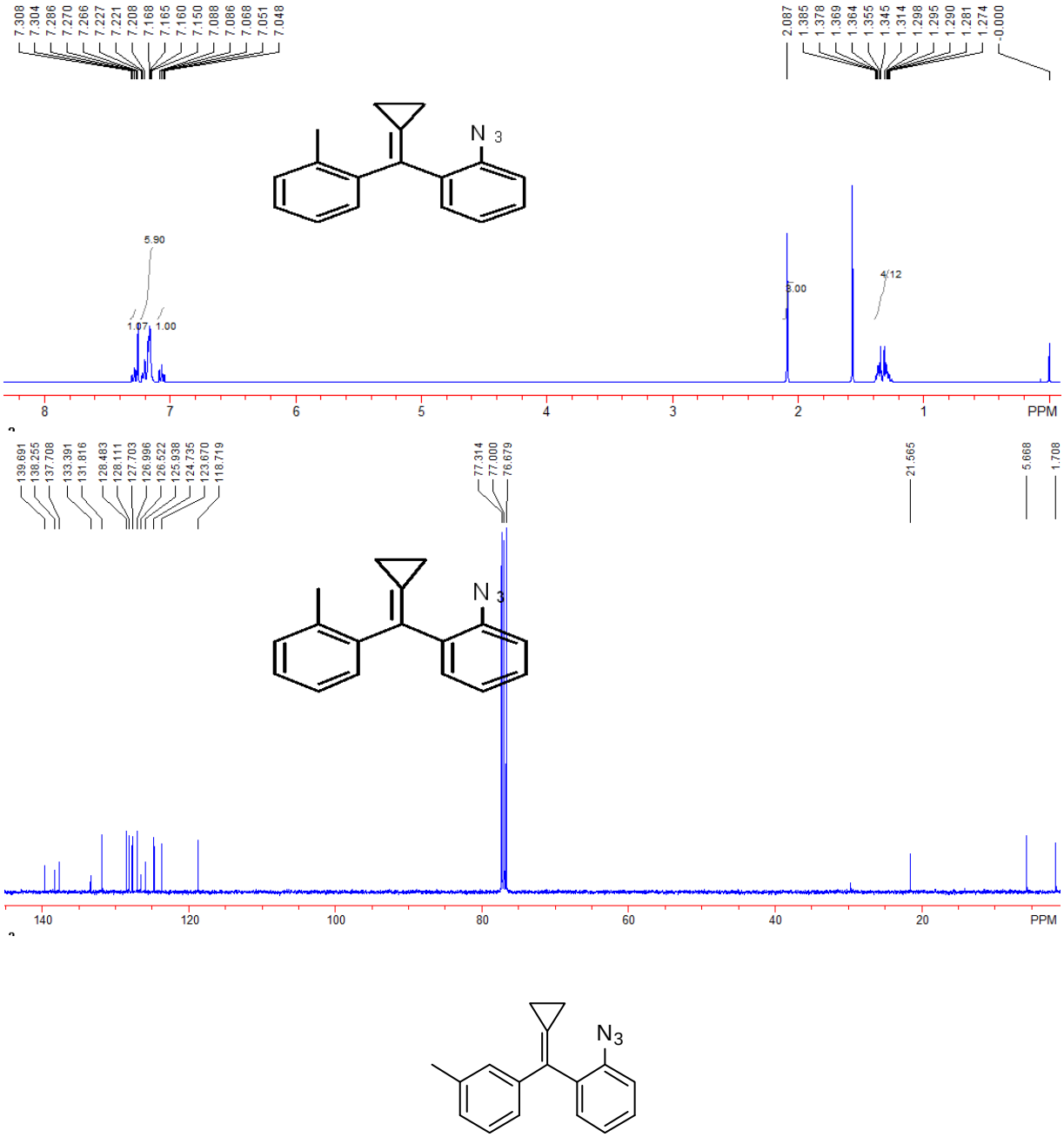
Compound 1a: 212 mg, 86%, A yellow solid, m.p. 95-97 ^{o}C; IR (CH_2Cl_2): ν 3052, 2977, 2121, 2086, 1493, 1288, 753 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 1.14-1.18 (m, 2H), 1.60-1.64 (m, 2H), 7.16-7.24 (m, 4H), 7.28-7.32 (m, 2H), 7.36-7.42 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 1.7, 5.6, 118.8, 124.8, 126.1, 126.4, 126.5, 126.9, 128.2, 128.5, 131.8, 133.3, 138.3, 139.7; MS (EI) m/z (%): 219 (38.3) [M-N_2^+], 218 (100.0), 204 (15.5), 189 (9.8), 165 (9.4), 115 (6.6), 108 (2.2), 89 (4.1); HRMS (EI) Calcd. for $C_{16}H_{13}N$ (M-N_2^+) requires 219.1048, found: 219.1042.





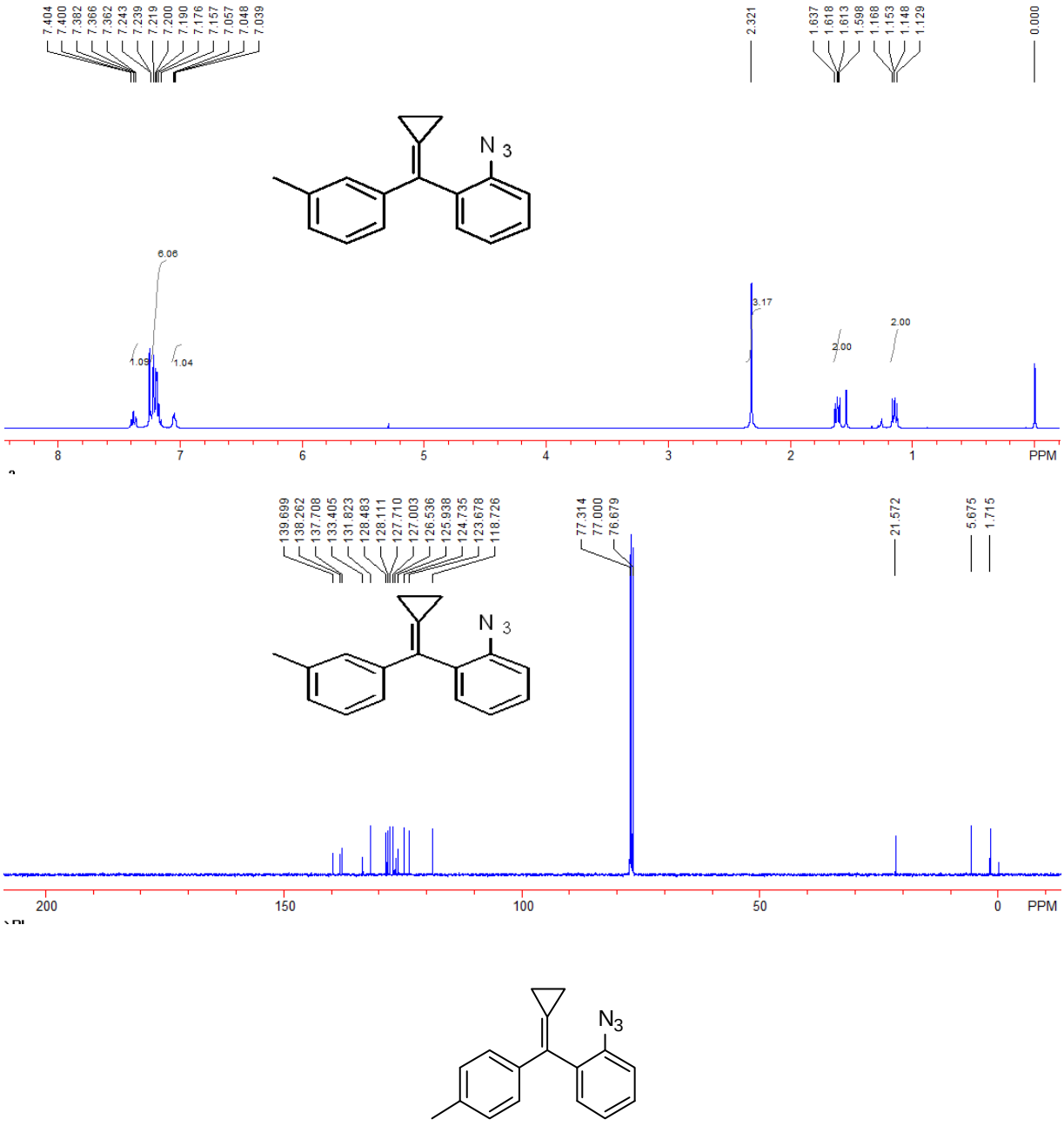


Compound 1b: 164 mg, 63%, A yellow solid, m.p. 56-58 ^{o}C; IR (CH_2Cl_2): ν 2971, 2118, 2082, 1484, 1287, 1039, 753 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 1.27-1.31 (m, 2H), 1.35-1.39 (m, 2H), 2.09 (s, 3H), 7.05-7.09 (m, 1H), 7.15-7.23 (m, 6H), 7.27-7.31 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 1.7, 5.7, 21.6, 118.7, 123.7, 124.7, 125.9, 126.5, 127.0, 127.7, 128.1, 128.5, 131.8, 133.4, 137.7, 138.3, 139.7; MS (EI) m/z (%): 233 (29.4) [M-N_2^+], 232 (51.9), 218 (79.7), 217 (100.0), 204 (13.1), 189 (11.0), 165 (10.0), 115 (12.1); HRMS (EI) Calcd. for $C_{17}H_{15}N$ (M-N_2^+) requires 233.1204, found: 233.1200.



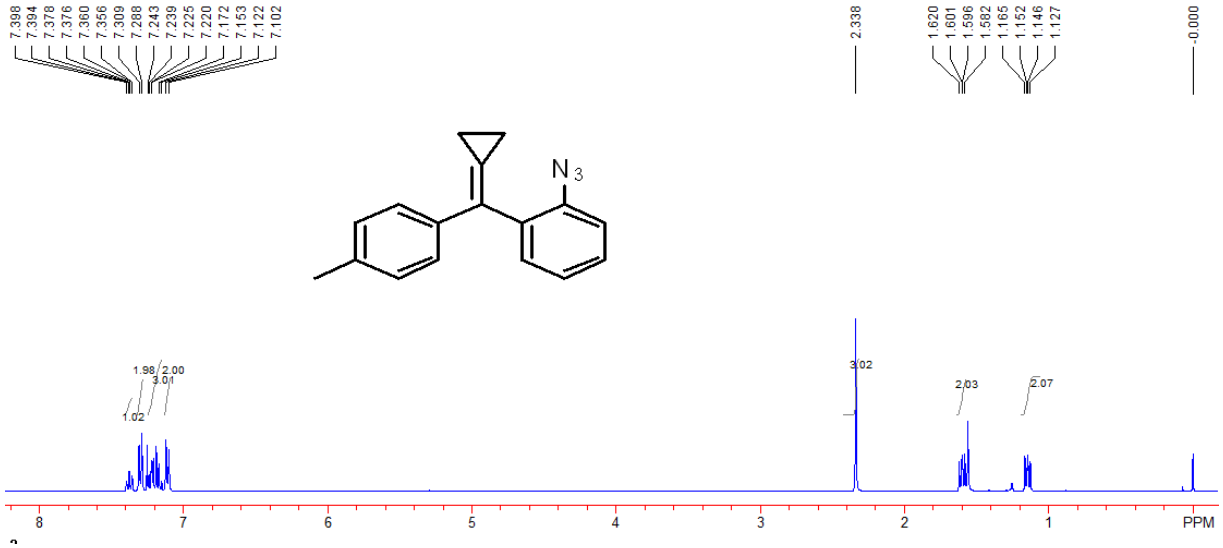
Compound 1c: 126 mg, 48%, A yellow solid, m.p. 60-62 ^{o}C; IR (CH_2Cl_2): ν 3051, 2971, 2119, 2083, 1485, 1287, 749 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 1.13-1.17 (m, 2H), 1.60-1.64

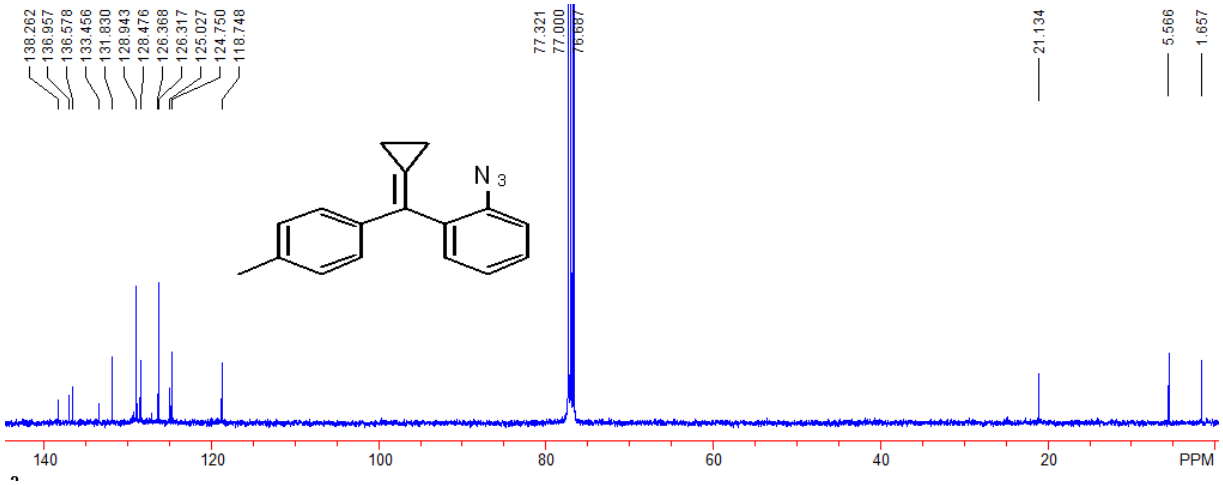
(m, 2H), 2.32 (s, 3H), 7.04-7.06 (m, 1H), 7.16-7.24 (m, 6H), 7.36-7.40 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 1.7, 5.7, 21.6, 118.7, 123.7, 124.7, 125.9, 126.5, 127.0, 127.7, 128.1, 128.5, 131.8, 133.4, 137.7, 138.3, 139.7; MS (EI) m/z (%): 233 (29.8) [M-N_2^+], 232 (49.7), 218 (80.8), 217 (100.0), 204 (13.4), 189 (11.6), 115 (12.6), 109 (14.4); HRMS (EI) Calcd. for $C_{17}H_{15}N$ (M-N_2^+) requires 233.1204, found: 233.1201.

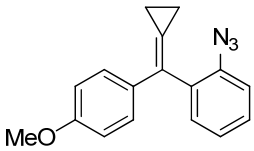


Compound 1d: 149 mg, 57%, A yellow solid, m.p. 63-65 ^{o}C; IR (CH_2Cl_2): ν 2971, 2120, 2087, 1485, 1293, 751 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 1.13-1.17 (m, 2H), 1.58-1.62 (m, 2H), 2.34 (s, 3H), 7.11 (d, *J* = 8.0 Hz, 2H), 7.15-7.24 (m, 3H), 7.30 (d, *J* = 8.4 Hz, 2H), 7.36-7.40 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 1.7, 5.6, 21.1, 118.7, 124.8, 125.0,

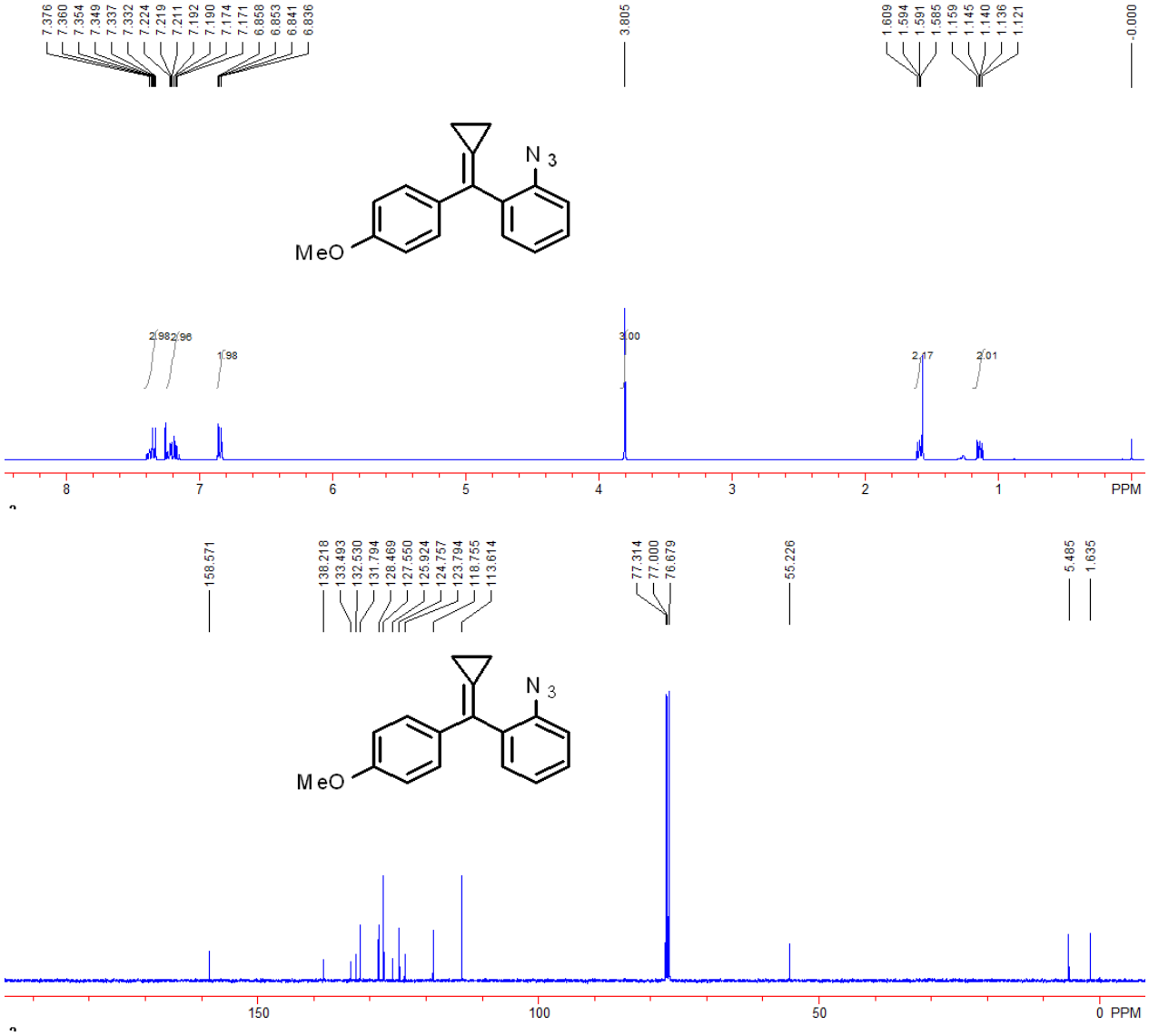
126.3, 126.4, 128.5, 128.9, 131.8, 133.5, 136.6, 137.0, 138.3; MS (EI) m/z (%): 233 (39.0) [M-N_2^+], 232 (72.9), 218 (67.4), 217 (100.0), 203 (8.7), 189 (11.4), 115 (12.2), 109 (14.1); HRMS (EI) Calcd. for $C_{17}H_{15}N$ (M-N_2^+) requires 233.1204, found: 233.1202.

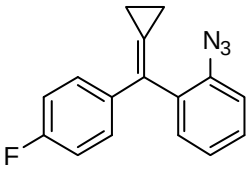




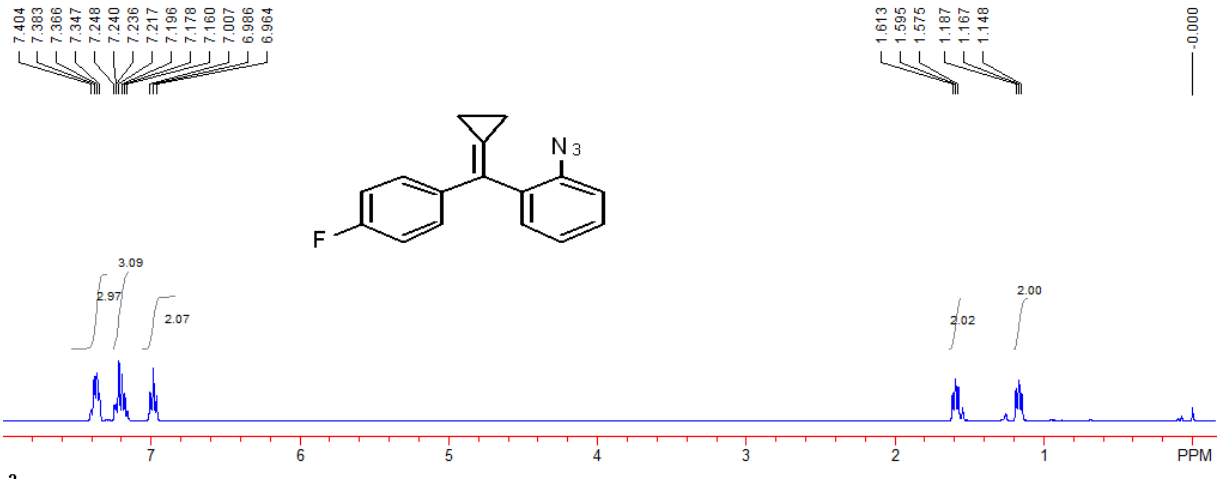


Compound 1e: 166 mg, 60%, A yellow solid, m.p. 68-70 ^{o}C; IR (CH_2Cl_2): ν 2970, 2120, 2087, 1602, 1483, 1300, 829 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 1.12-1.16 (m, 2H), 1.59-1.61 (m, 2H), 3.81 (s, 3H), 6.84-6.86 (m, 2H), 7.17-7.24 (m, 3H), 7.33-7.38 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 1.6, 5.5, 55.2, 113.6, 118.8, 123.8, 124.8, 125.9, 127.6, 128.5, 131.8, 132.5, 133.5, 138.2, 158.6; MS (ESI) *m/z*: 278.1 (M+H^+, 100); HRMS (ESI) Calcd. for $C_{17}H_{16}N_3O^+$ requires: 278.1293, found: 278.1298.





Compound 1f: 167 mg, 63%, A yellow solid, m.p. 88-90 ^{o}C; IR (CH_2Cl_2): ν 2120, 2087, 1506, 1486, 1296, 752 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 1.15-1.19 (m, 2H), 1.58-1.61 (m, 2H), 6.99 (dd, $J_1 = J_2 = 8.4$ Hz, 2H), 7.16-7.25 (m, 3H), 7.35-7.40 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 1.8, 5.5, 115.0 (d, $J_{C\text{-}F} = 21.2$ Hz), 118.8, 124.8, 125.6, 125.72 (d, $J_{C\text{-}F} = 1.5$ Hz), 127.9 (d, $J_{C\text{-}F} = 8.0$ Hz), 128.7, 131.7, 133.0, 135.9 (d, $J_{C\text{-}F} = 3.0$ Hz), 138.2, 161.8 (d, $J_{C\text{-}F} = 244.3$ Hz); ^{19}F NMR (376 MHz, $CDCl_3$, $CFCl_3$): δ -115.7 (s); MS (EI) m/z (%): 237 (39.3) [M-N_2^+], 236 (100.0), 235 (66.6), 222 (13.4), 217 (7.4), 207 (7.9), 183 (10.7), 118 (10.0); HRMS (EI) Calcd. for $C_{16}H_{12}FN$ (M-N_2^+) requires 237.0954, found: 237.0956.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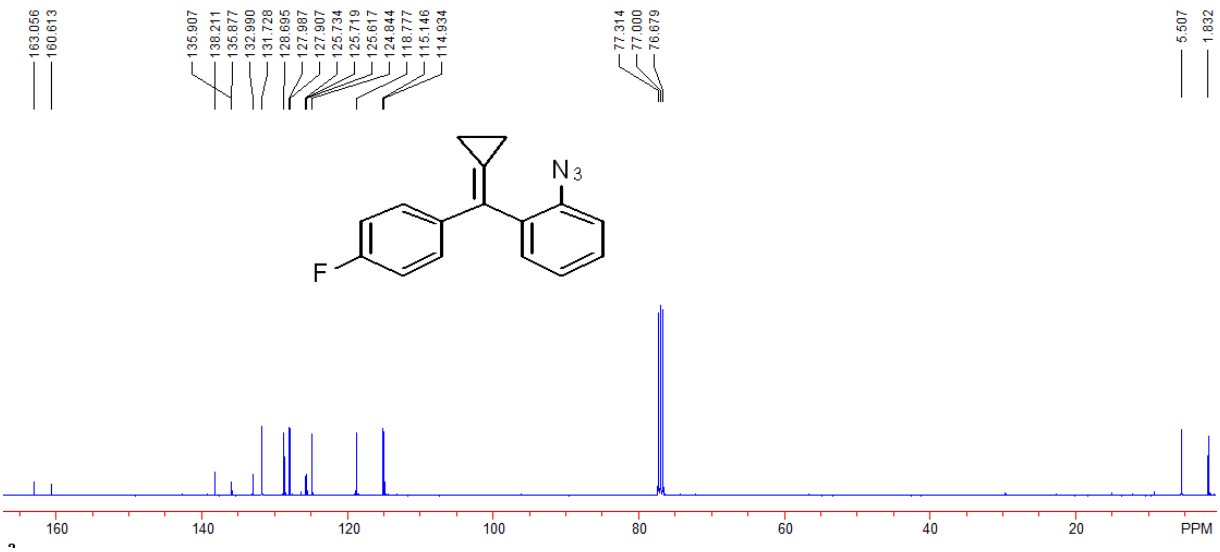
PPM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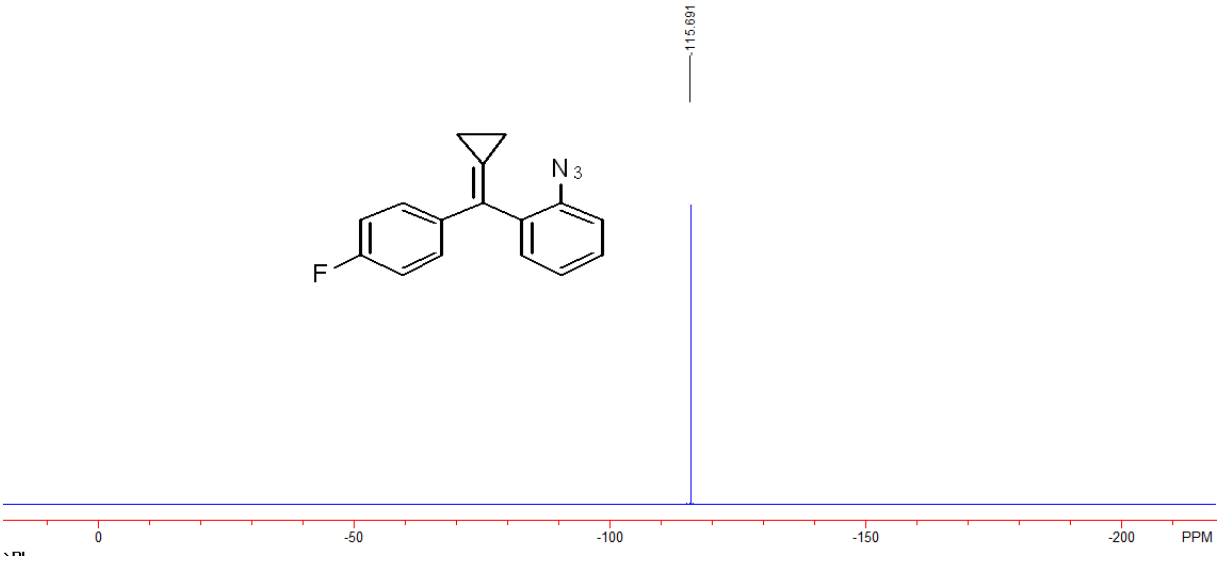
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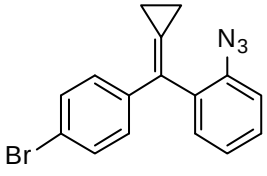
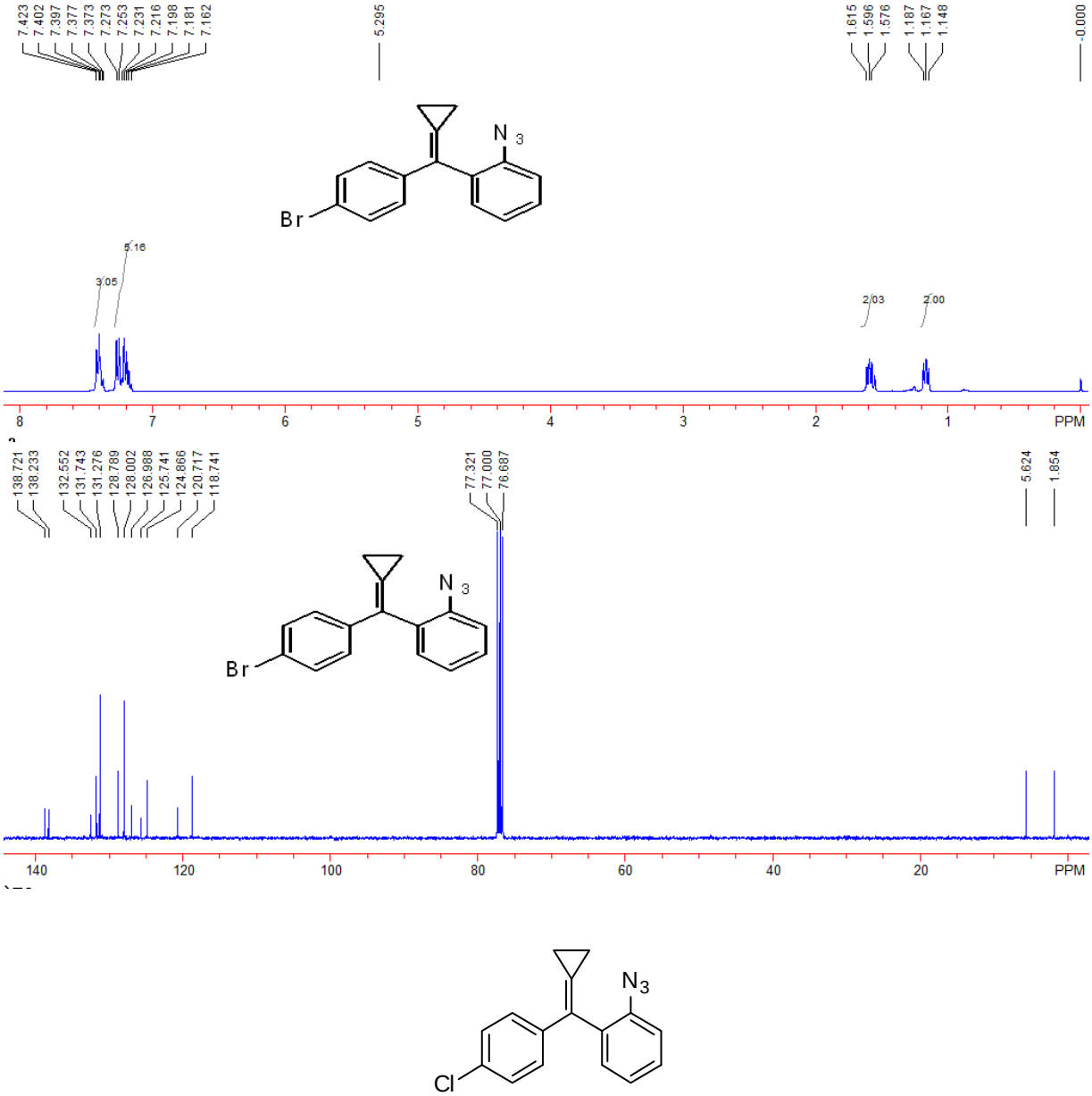
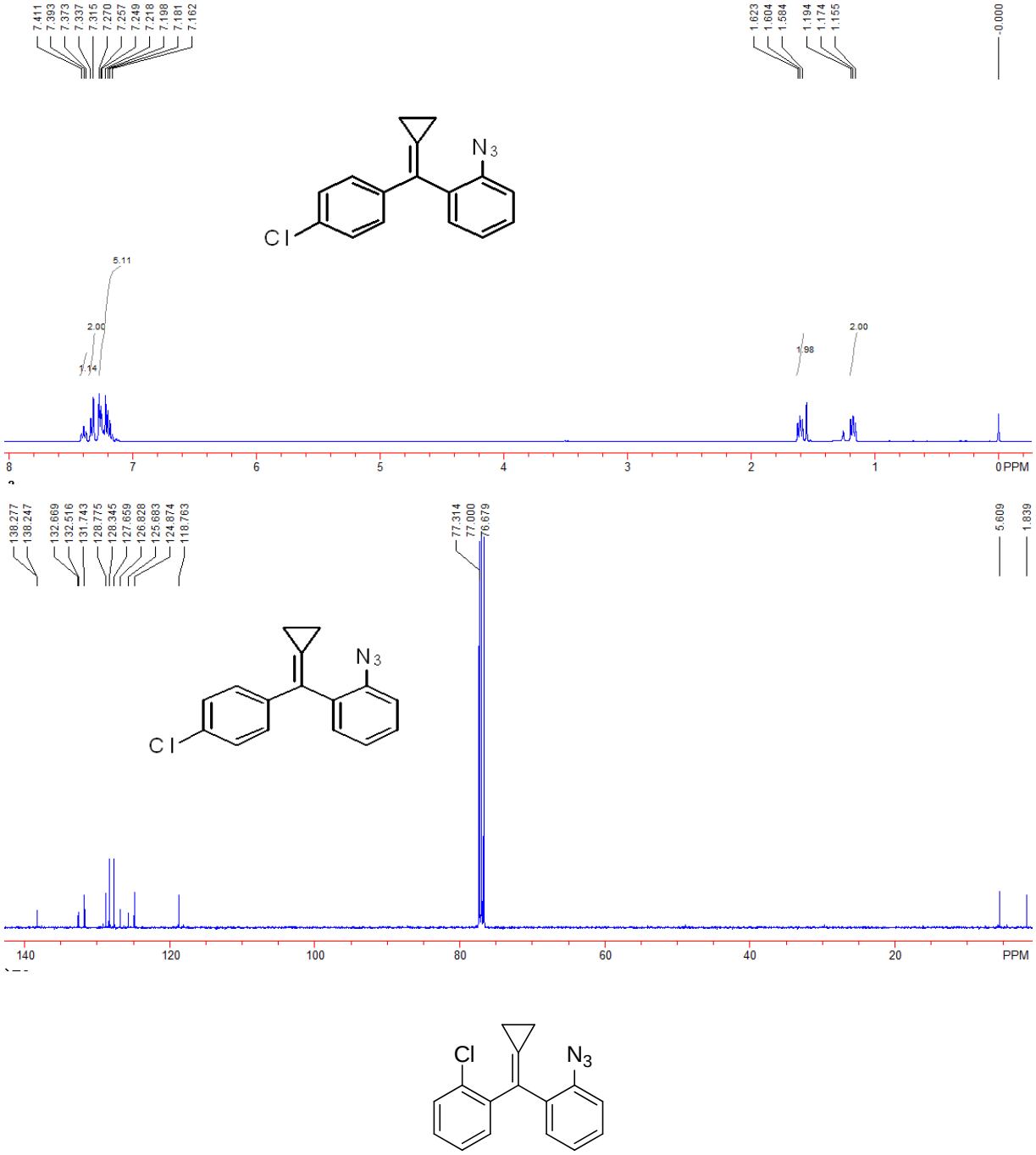

N3
Br

Compound 1g: 204 mg, 67%, A yellow solid, m.p. 105-107 ^{o}C; IR (CH_2Cl_2): ν 2121, 2086, 1573, 1485, 1290, 752 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 1.15-1.19 (m, 2H), 1.58-1.62 (m, 2H), 7.16-7.27 (m, 5H), 7.37-7.42 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 1.9, 5.6, 118.7, 120.7, 124.9, 125.7, 127.0, 128.0, 128.8, 131.3, 131.7, 132.6, 138.2, 138.7; MS (EI) m/z (%): 297 (11.4) [M-N_2^+], 218 (64.4), 217 (100), 203 (9.2), 189 (16.4), 165 (6.9), 109 (14.2), 95 (8.3); HRMS (EI) Calcd. for $C_{16}H_{12}BrN$ (M-N_2^+) requires 297.0153, found: 297.0151.



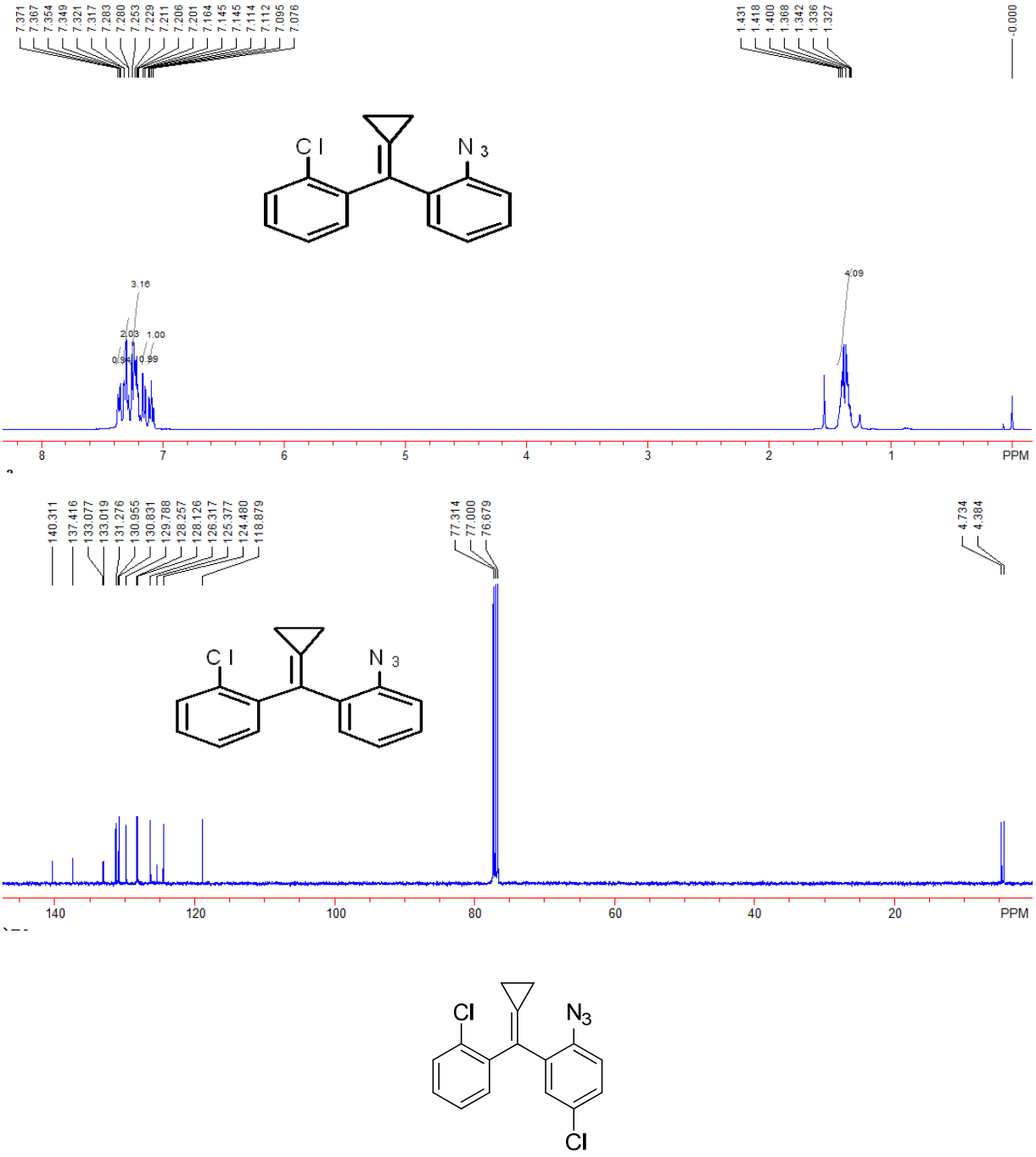
Compound 1h: 203 mg, 66%, A yellow solid, m.p. 93-95 ^{o}C; IR (CH_2Cl_2): ν 2978, 2120, 2085, 1488, 1292, 1092, 752 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 1.16-1.19 (m, 2H), 1.58-1.62 (m, 2H), 7.16-7.27 (m, 5H), 7.33 (d, J = 8.8 Hz, 2H), 7.39 (dd, $J_1 = J_2$ = 7.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 1.8, 5.6, 118.8, 124.9, 125.7, 126.8, 127.7, 128.3, 128.8, 131.7, 132.5,

132.7, 138.2, 138.3; MS (EI) m/z (%): 253 (20.4) [M-N_2^+], 252 (24.5), 218 (66.1), 217 (100.0), 189 (15.0), 163 (7.5), 135 (10.1), 108 (5.1); HRMS (EI) Calcd. for $C_{16}H_{12}ClN$ (M-N_2^+) requires 253.0658, found: 253.0655.



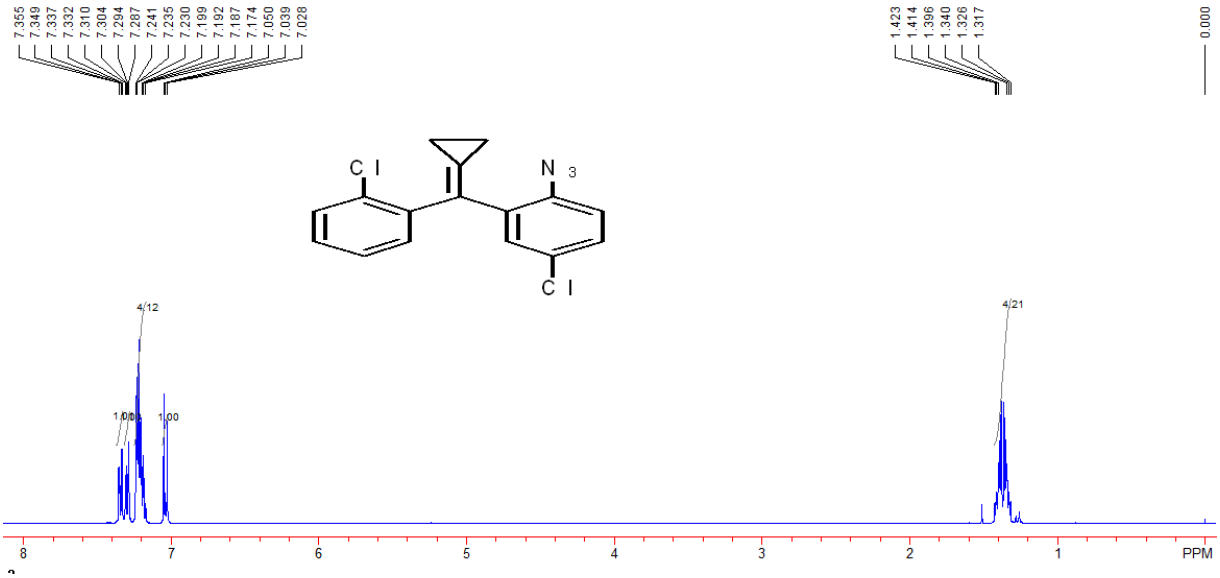
Compound 1i: 218 mg, 77%, A yellow solid, m.p. 74-76 ^oC; IR (CH_2Cl_2): ν 3048, 2974, 2120, 2085, 1485, 1290, 751 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$, TMS): δ 1.33-1.43 (m, 4H), 7.08-7.11 (m, 1H), 7.15-7.16 (m, 1H), 7.20-7.25 (m, 3H), 7.28-7.32 (m, 2H), 7.35-7.37 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 4.4, 4.7, 118.9, 124.5, 125.4, 126.3, 128.1, 128.3, 129.8, 130.8, 131.0, 131.3, 133.0, 133.1, 137.4, 140.3; MS (EI) m/z (%): 253 (16.4) [M-N_2^+], 218 (84.5), 217 (100.0),

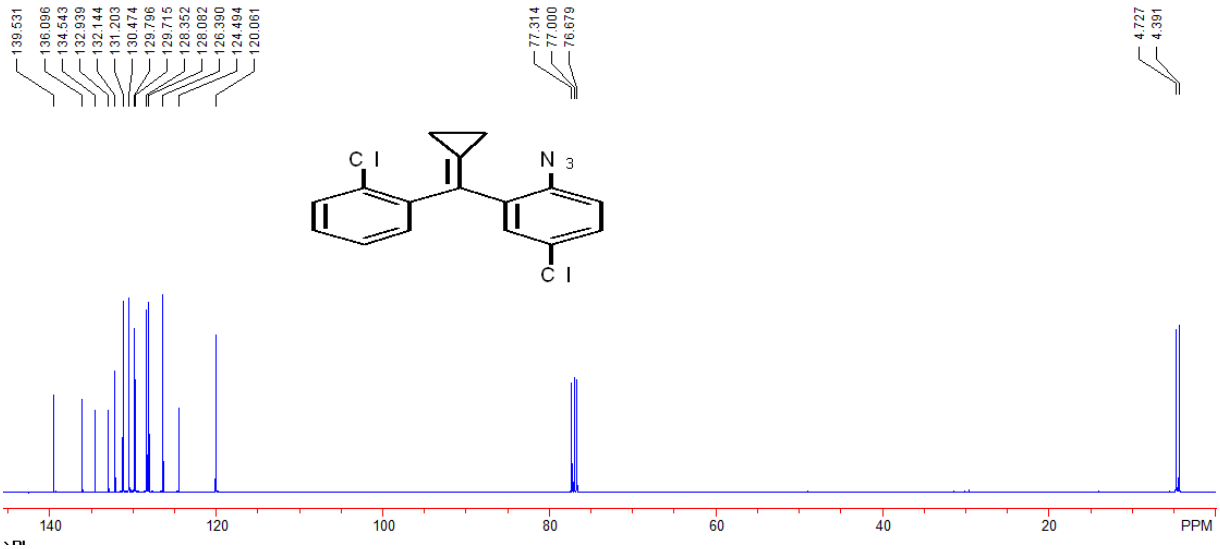
203 (6.5), 189 (15.9), 165 (7.0), 109 (12.0), 95 (8.0); HRMS (EI) Calcd. for $C_{16}H_{12}ClN$ ($M-N_2^+$) requires 253.0658, found: 253.0652.

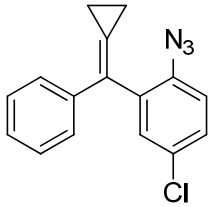


Compound 1j: 233 mg, 74%, A yellow solid, m.p. 77-79 ^{o}C; IR (CH_2Cl_2): ν 3055, 2978, 2121, 2091, 1478, 1295, 740 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 1.32-1.42 (m, 4H), 7.03-7.05 (m, 1H), 7.17-7.24 (m, 4H), 7.30 (dd, J_1 = 6.8 Hz, J_2 = 2.4 Hz, 1H), 7.34 (dd, J_1 = 6.8 Hz, J_2 = 2.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 4.4, 4.7, 120.1, 124.5, 126.4, 128.1, 128.4, 129.7, 129.8, 130.5, 131.2, 132.1, 132.9, 134.5, 136.1, 139.5; MS (EI) m/z (%): 287 (10.6)

[M-N_2^+], 252 (46.5), 231 (19.5), 217 (100.0), 189 (20.2), 177 (8.7), 108 (12.3), 95 (12.8); HRMS (EI) Calcd. for $C_{16}H_{11}Cl_2N$ (M-N_2^+) requires 287.0269, found: 287.0267.

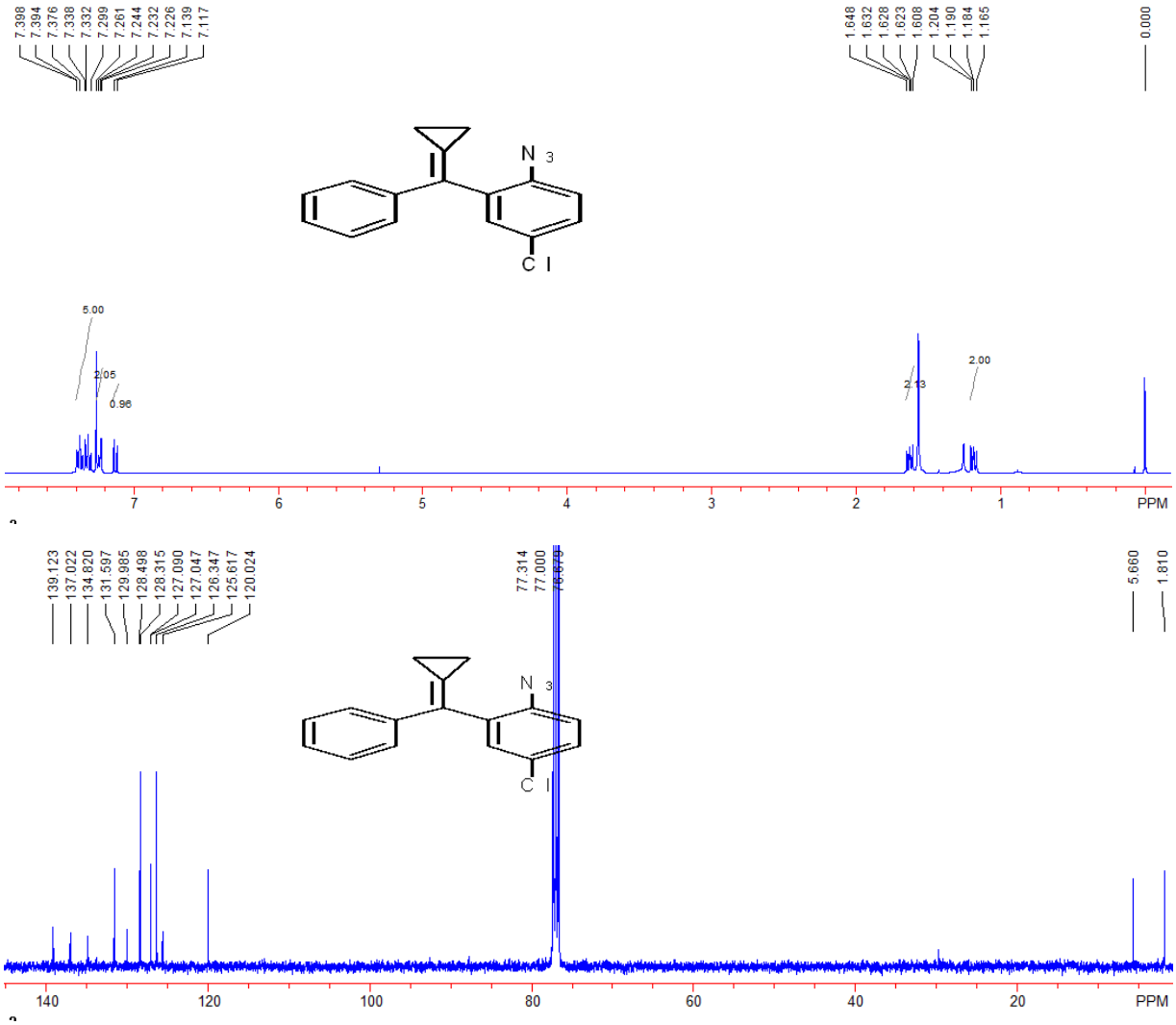


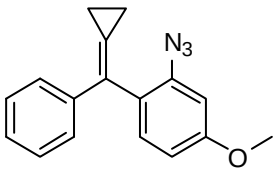




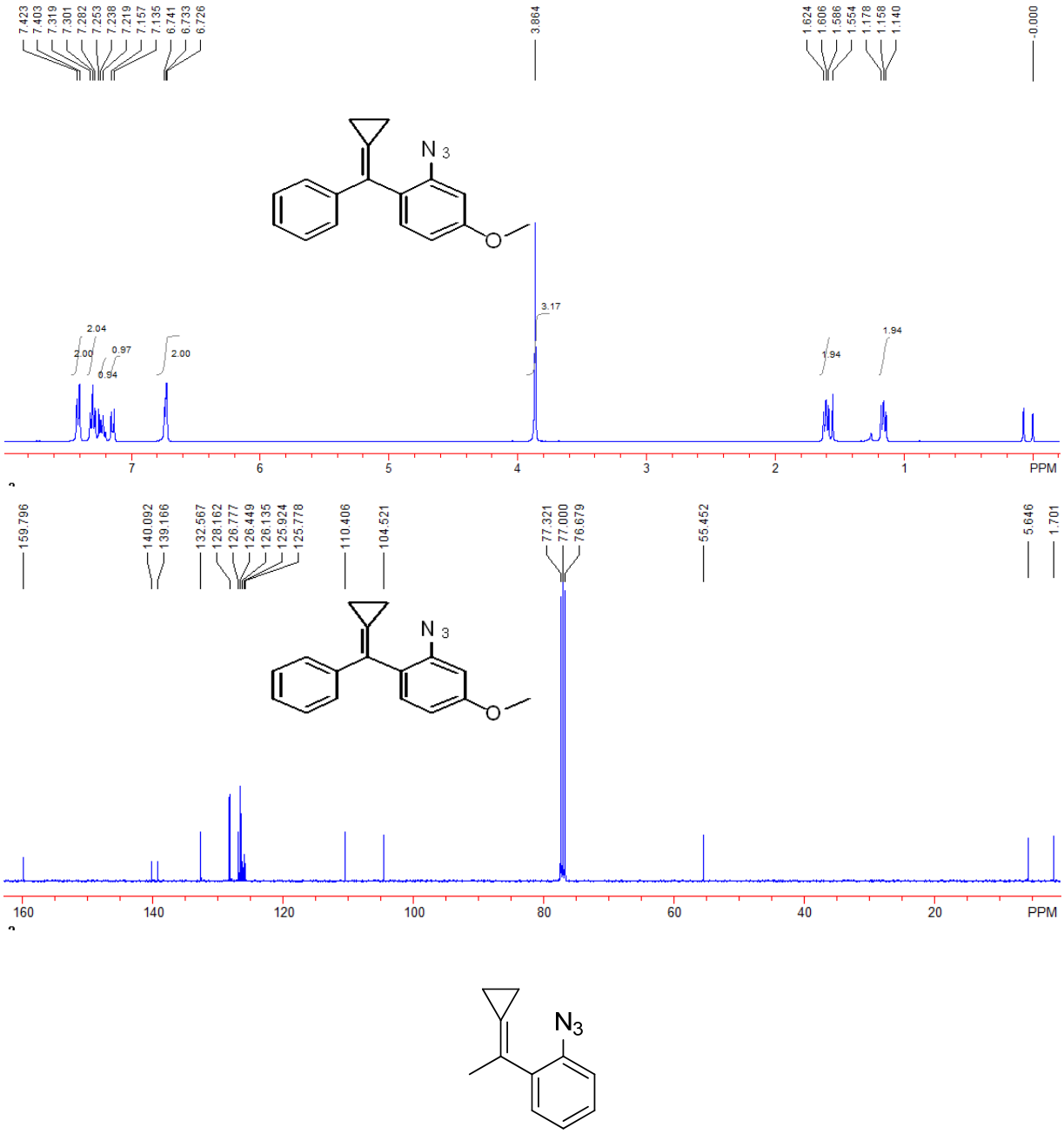
Compound 1k: 266 mg, 95%, A yellow solid, m.p. 85-87 ^oC; IR (CH_2Cl_2): ν 3084, 2919, 2124, 2093, 1493, 1299, 766 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$, TMS): δ 1.17-1.20 (m, 2H), 1.61-1.65 (m, 2H), 7.13 (d, *J* = 8.8 Hz, 1H), 7.23-7.26 (m, 2H), 7.30-7.40 (m, 5H); ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 1.8, 5.7, 120.0, 125.6, 126.3, 127.0, 127.1, 128.3, 128.5, 130.0, 131.6, 134.8, 137.0, 139.1; MS (EI) m/z (%): 253 (31.8) [M-N_2^+], 218 (42.1), 217 (100.0), 203 (9.7), 189

(16.5), 165 (8.1), 109 (14.2), 95 (9.4); HRMS (EI) Calcd. for $C_{16}H_{12}ClN$ ($M-N_2^+$) requires 253.0658, found: 253.0659.

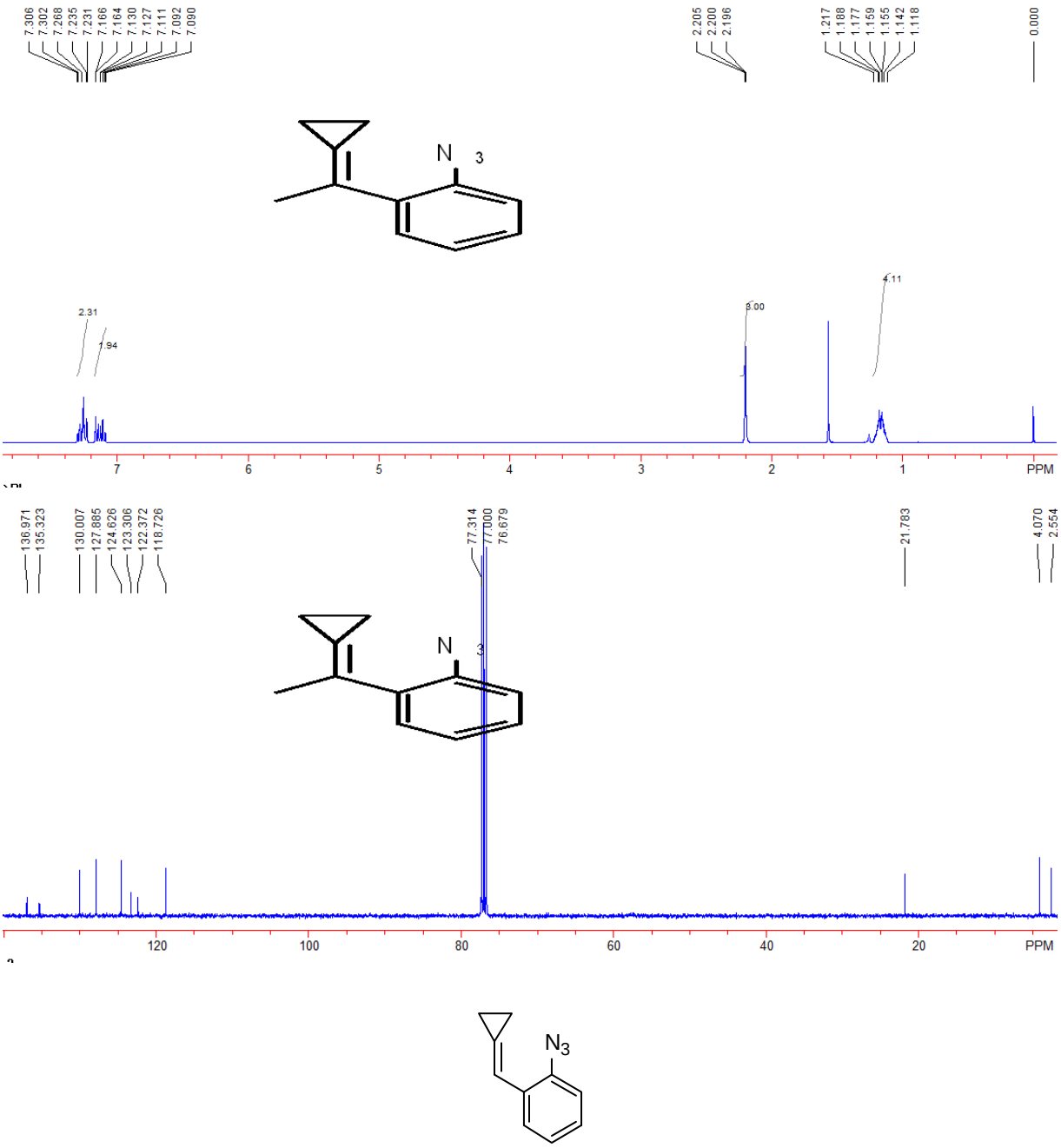




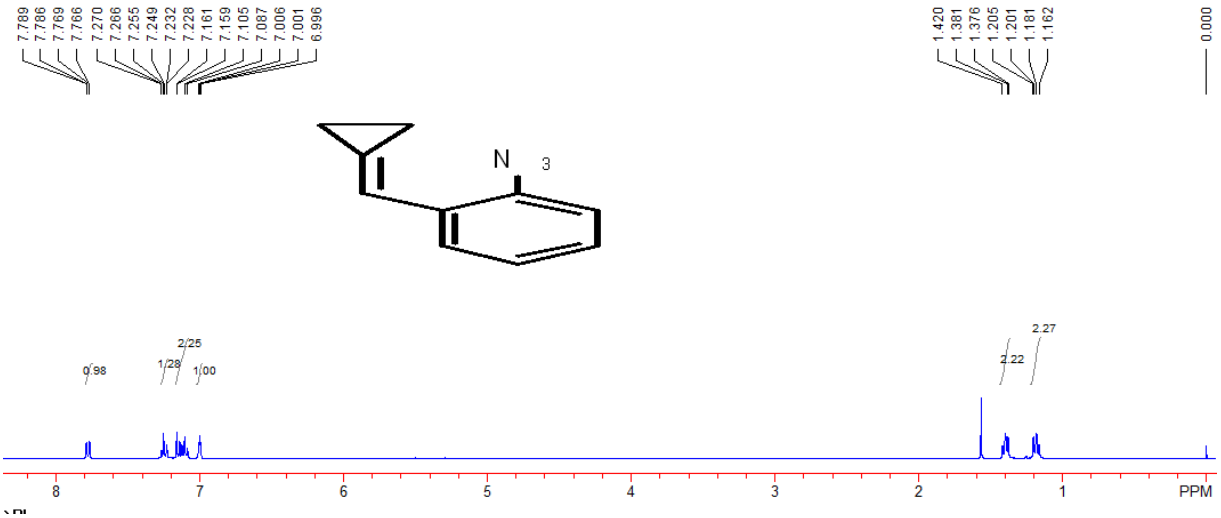
Compound 1l: 186 mg, 67%, A yellow solid, m.p. 68-70 ^{o}C; IR (CH_2Cl_2): ν 2126, 1606, 1504, 1229, 1036, 766 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 1.14-1.18 (m, 2H), 1.55-1.62 (m, 2H), 3.86 (s, 3H), 6.73-6.74 (m, 2H), 7.14 (d, J = 8.8 Hz, 1H), 7.22-7.25 (m, 1H), 7.30 (dd, J_1 = J_2 = 7.6 Hz, 2H), 7.41 (d, J = 8.0 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 1.7, 5.6, 55.5, 104.5, 110.4, 125.8, 125.9, 126.1, 126.4, 126.8, 128.2, 132.6, 139.2, 140.1, 159.8; MS (EI) m/z (%): 277 (0.8) [M^+], 248 (100.0), 234 (56.0), 217 (24.5), 204 (67.0), 191 (23.9), 178 (27.4), 165 (19.2); HRMS (EI) Calcd. for $C_{17}H_{15}N_3O$ (M^+) requires 277.1215, found: 277.1218.



Compound 1m: 98 mg, 53%, A colorless liquid; IR (CH_2Cl_2): ν 3403, 2921, 2106, 2078, 1488, 1290, 749cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 1.12-1.22 (m, 4H), 2.20 (t, J = 2.0 Hz, 3H), 7.09-7.17 (m, 2H), 7.23-7.31 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 2.6, 4.1, 21.8, 118.7, 122.4, 123.3, 124.6, 127.9, 130.0, 135.3, 137.0; MS (EI) m/z (%): 157 (5.2) [M-N_2^+], 156 (7.6), 145 (11.1), 144 (100.0), 143 (14.1), 128 (7.0), 115 (7.2), 77 (7.1); HRMS (EI) Calcd. for $C_{11}H_{11}N$ (M-N_2^+) requires 157.0891, found: 157.0896.



Compound 1n: 157 mg, 92%, A colorless liquid; IR (CH_2Cl_2): ν 2974, 2119, 1575, 1485, 1295, 748 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$, TMS): δ 1.16-1.21 (m, 2H), 1.38-1.42 (m, 2H), 7.00 (t, J = 2.0 Hz, 1H), 7.09-7.16 (m, 2H), 7.23-7.27 (m, 1H), 7.78 (dd, J_1 = 1.2 Hz, J_2 = 0.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 0.7, 4.0, 112.4, 118.3, 124.7, 126.2, 126.9, 127.8, 129.7, 136.5; MS (EI) m/z (%): 171 (8.9) [M^+], 143 (72.2), 130 (21.9), 115 (100.0), 103 (12.5), 89 (20.5), 77 (18.8), 63 (15.5); HRMS (EI) Calcd. for $C_{10}H_9N_3$ (M^+) requires 171.0796, found: 171.0801.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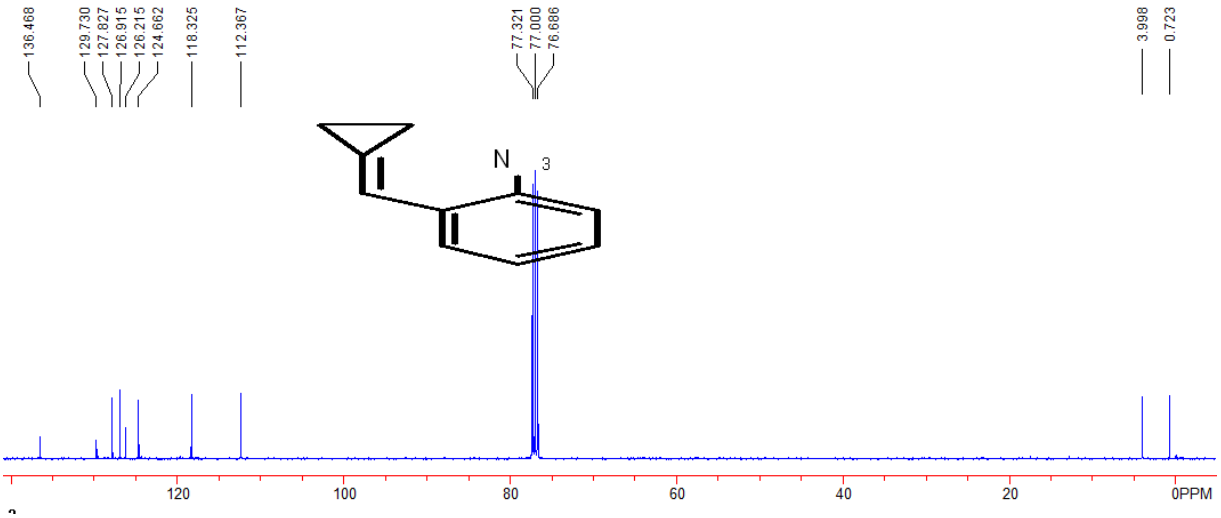
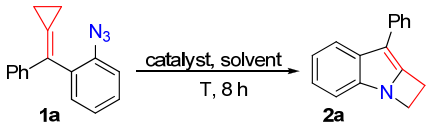
7.786
7.769
7.766
7.270
7.266
7.255
7.249
7.232
7.228
7.161
7.159
7.105
7.087
7.006
7.001
6.996
1.420
1.381
1.376
1.205
1.201
1.181
1.162
0.000
N
3
0.98
2.25
1.28
1.00
2.22
2.27
8
7
6
5
4
3
2
1
PPM


136.468
129.730
127.827
126.915
126.215
124.662
118.325
112.367
77.321
77.000
76.686
3.998
0.723
N
3
120
100
80
60
40
20
0PPM

Optimization of the reaction conditions of rhodium-catalyzed reaction of 1a (Table S1)

Table S1 Optimization of the reaction conditions of rhodium-catalyzed intramolecular reaction of **1a**



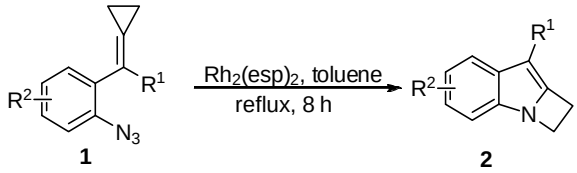
1a **2a**

entry[a]	catalyst	solvent	T/°C	yield/%[b]
1	$Rh_2(OAc)_4$	toluene	80	18
2	$Rh_2(Piv)_4$	toluene	80	22
3	$Rh_2(esp)_2$	toluene	80	30
4	$Rh_2(esp)_2$	toluene	90	56
5	***$Rh_2(esp)_2$***	***toluene***	***110***	***90***
6	-	chlorobenzene	120	-
7	-	chlorobenzene	140	40

[a] Reaction conditions: **1a** (0.2 mmol), catalyst (3 mol %), solvent (1.0 mL). [b] Isolated yield. Piv = pivalate. esp = a,a,a',a'-tetramethyl-1,3-benzenedipropionic acid.

We initially investigated the reaction of 1-azido-2-(cyclopropylidene(phenyl)methyl)benzene **1a** by variation of catalysts, solvents and temperature (Table S1). When $Rh_2(OAc)_4$, $Rh_2(Piv)_4$ and $Rh_2(esp)_2$ were used as catalysts, **2a** could be furnished in 18-30% yields (Table S1, entries 1-3). Its structure has been unambiguously determined by X-ray diffraction. $Rh_2(esp)_2$ was chosen as the best catalyst in this reaction. Increasing the reaction temperature to 90 °C improved the yield of **2a** to 56% (Table S1, entry 4). Further increasing the reaction temperature to 110 °C, **2a** could be afforded in 90% yield (Table S1, entry 5). We also found that running the reaction in chlorobenzene at 120 °C without catalyst, no reaction took place (Table S1, entry 6), but, **2a** could be delivered in 40% yield upon heating at 140 °C, suggesting that a thermal-induced process might be involved at high temperature (> 140 °C) (Table S1, entry 7).

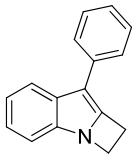
General procedure for the synthesis of compounds 2



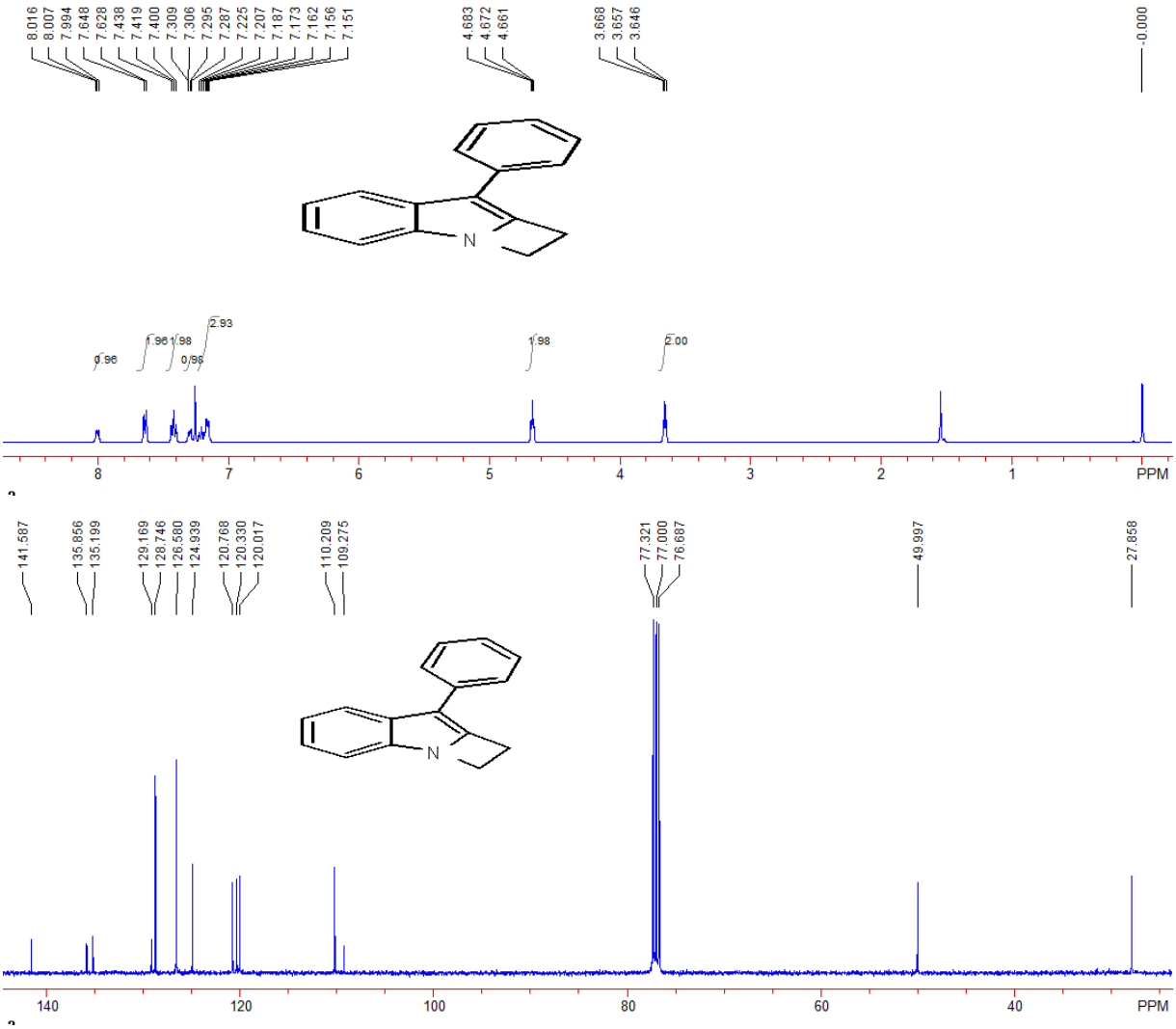
1 **2**

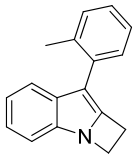
A solution of compound **1** (0.2 mmol) and $Rh_2(esp)_2$ (4.5 mg, 0.006 mmol) in dry toluene (1 mL) was stirred at 110 ^oC for 8 h. Then the solvent was removed under reduced pressure and the residue was purified by silica gel flash chromatography (eluent: petroleum ether / ethyl acetate = 30 / 1) to afford the product in moderate to high yield.

Spectroscopic data for all products 2

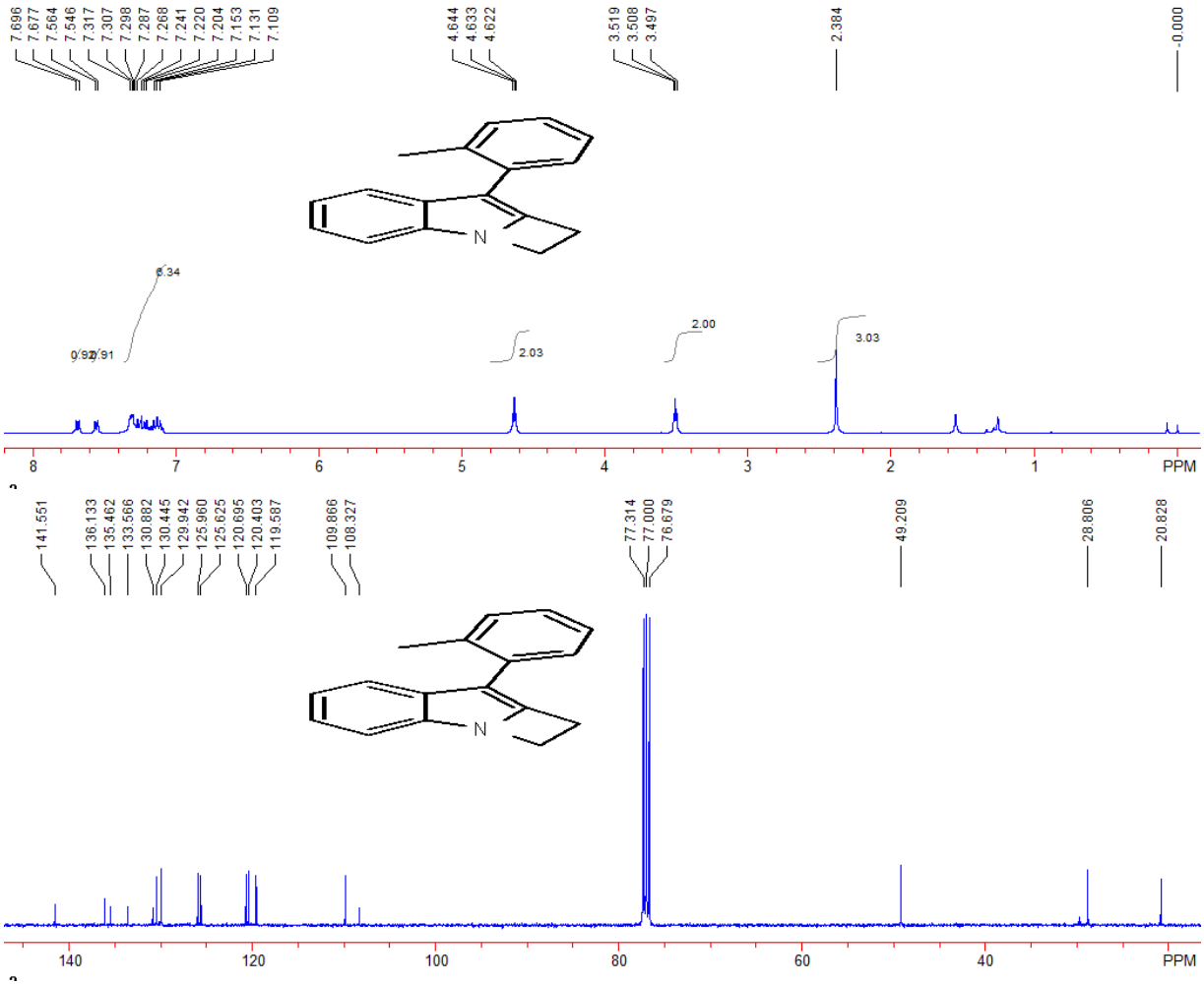


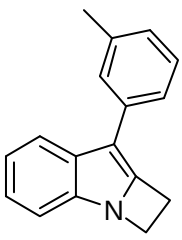
Compound 2a: 39 mg, 90%, A yellow solid, m.p. 110-112 ^{o}C; IR (CH_2Cl_2): ν 3053, 2954, 1602, 1439, 1179, 1050, 753, 696 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 3.66 (t, J = 4.4 Hz, 2H), 4.67 (t, J = 4.4 Hz, 2H), 7.15-7.23 (m, 3H), 7.29-7.31 (m, 1H), 7.42 (dd, J_1 = J_2 = 7.6 Hz, 2H), 7.64 (d, J = 8.0 Hz, 2H), 8.00-8.02 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 27.9, 50.0, 109.3, 110.2, 120.0, 120.3, 120.8, 124.9, 126.6, 128.7, 129.2, 135.2, 135.9, 141.6; MS (ESI) *m/z*: 220.1 (M+H^{+}, 100); HRMS (ESI) Calcd. for $C_{16}H_{14}N^{+}$ requires: 200.1121, found: 200.1129.



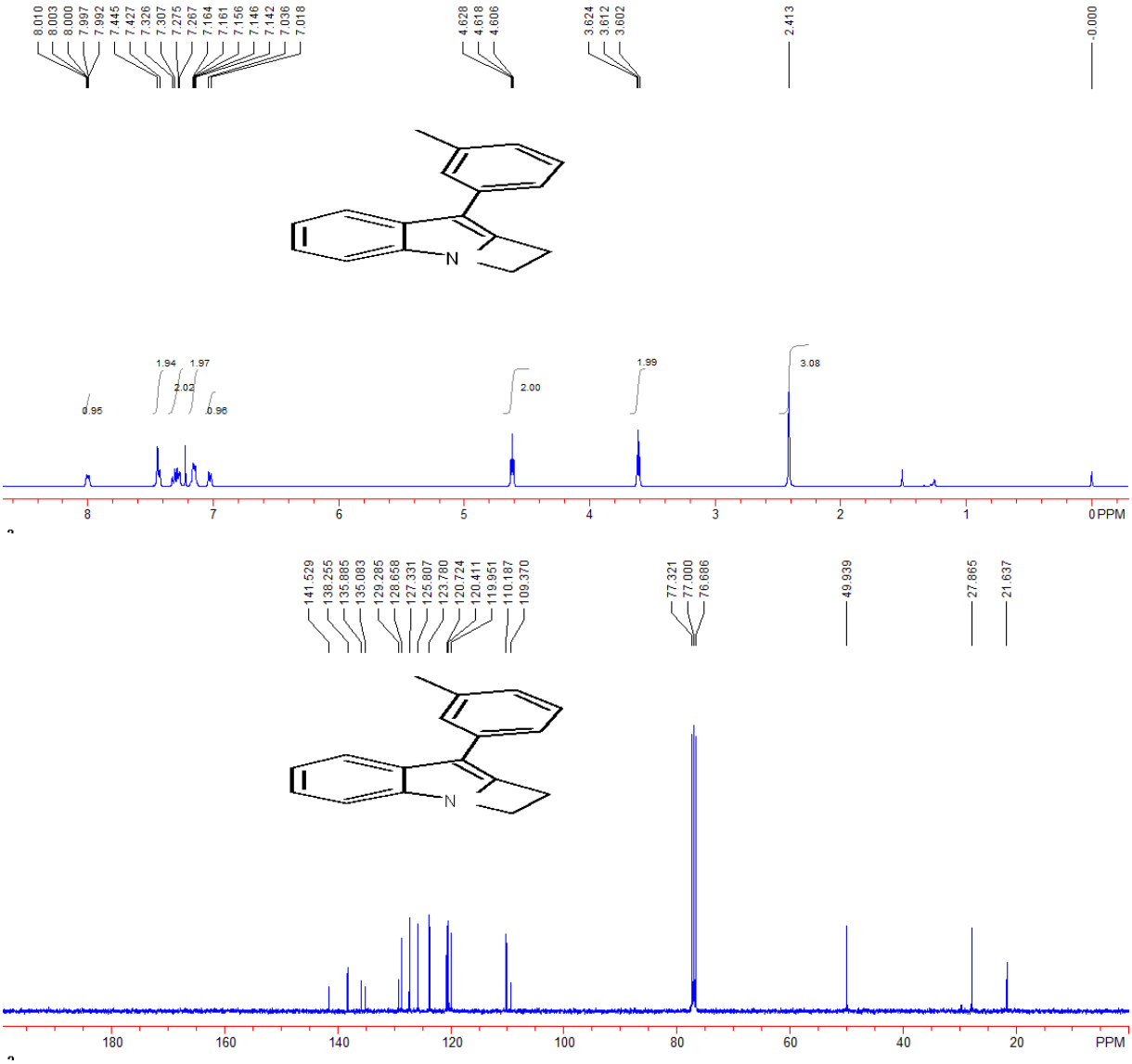


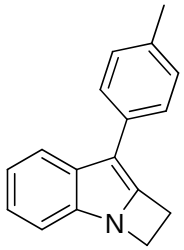
Compound 2b: 36 mg, 77%, A yellow solid, m.p. 104-106 ^{o}C; IR (CH_2Cl_2): ν 3052, 2955, 1604, 1438, 1180, 1041, 763 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 2.38 (s, 3H), 3.51 (t, *J* = 4.4 Hz, 2H), 4.63 (t, *J* = 4.4 Hz, 2H), 7.11-7.32 (m, 6H), 7.56 (d, *J* = 7.2 Hz, 1H), 7.69 (d, *J* = 7.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 20.8, 28.8, 49.2, 108.3, 109.9, 119.6, 120.4, 120.7, 125.6, 126.0, 129.9, 130.4, 130.9, 133.6, 135.5, 136.1, 141.6; MS (ESI) *m/z*: 234.1 ($M+H^+$, 100); HRMS (ESI) Calcd. for $C_{17}H_{16}N^+$ requires: 234.1277, found: 234.1284.



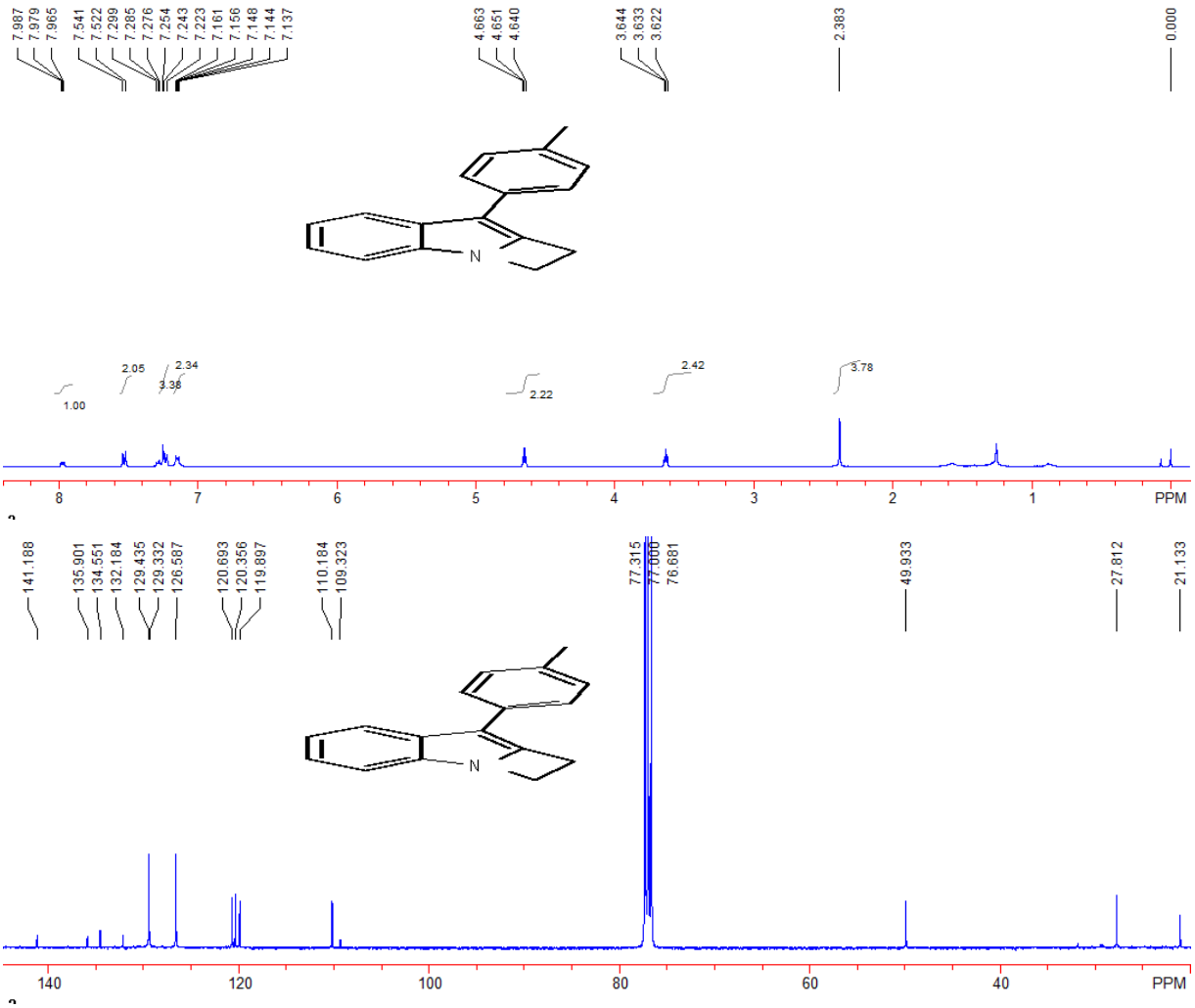


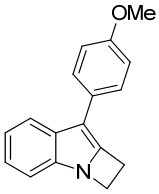
Compound 2c: 35 mg, 75%, A yellow solid, m.p. 100-102 ^{o}C; IR (CH_2Cl_2): ν 3052, 2954, 1604, 1437, 1149, 1050, 740 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 2.41 (s, 3H), 3.61 (t, *J* = 4.0 Hz, 2H), 4.62 (t, *J* = 4.0 Hz, 2H), 7.03 (d, *J* = 7.2 Hz, 1H), 7.14-7.16 (m, 2H), 7.27-7.33 (m, 2H), 7.43-7.45 (m, 2H), 7.99-8.01 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 21.6, 27.9, 49.9, 109.4, 110.2, 120.0, 120.4, 120.7, 123.8, 125.8, 127.3, 128.7, 129.3, 135.1, 135.9, 138.3, 141.5; MS (EI) m/z (%): 233 (100.0) [M^+], 232 (66.1), 218 (95.4), 204 (17.1), 189 (10.9), 178 (10.8), 115 (11.7), 109 (15.2); HRMS (EI) Calcd. for $C_{17}H_{15}N$ (M^+) requires 233.1204, found: 233.1207.



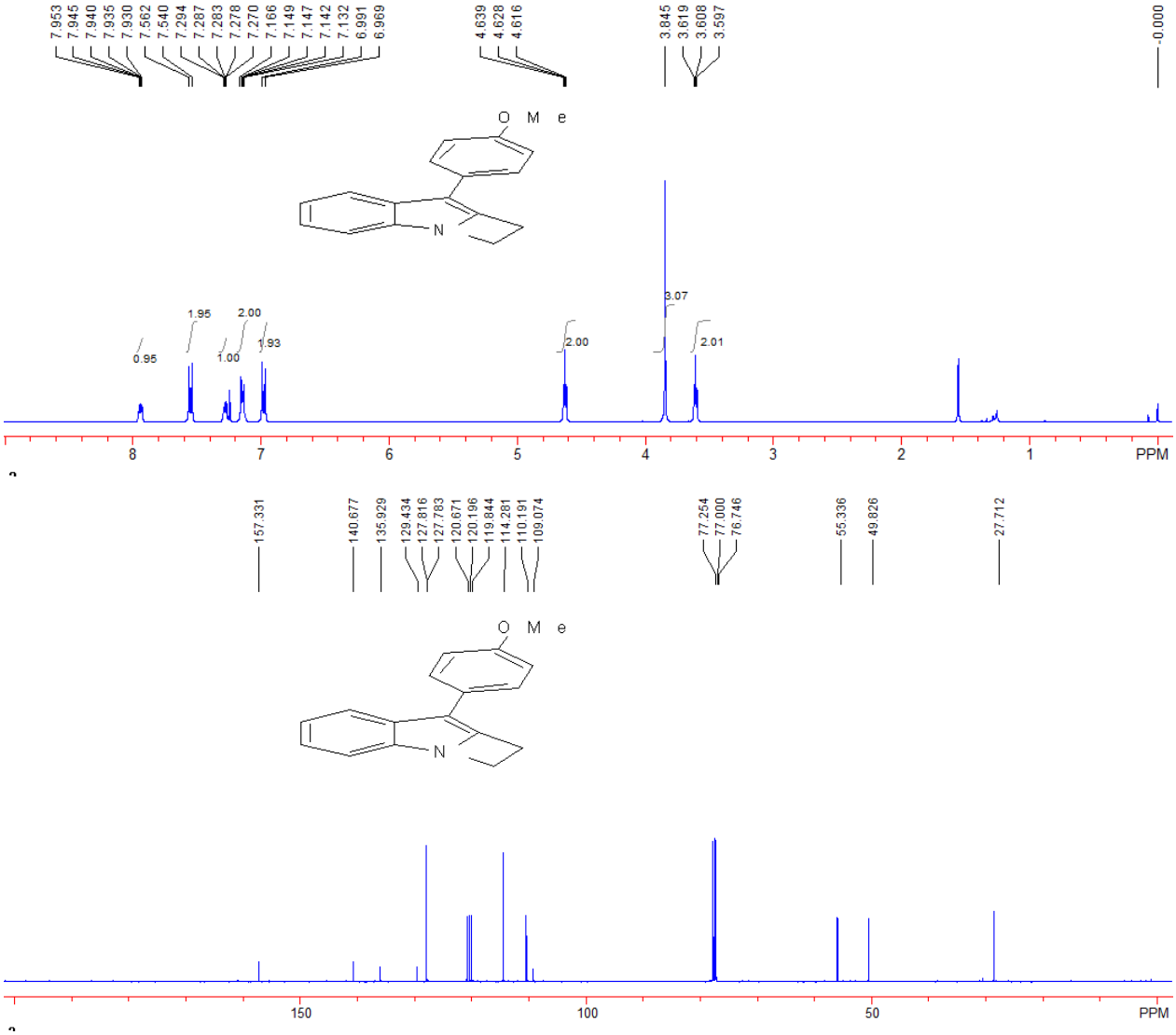


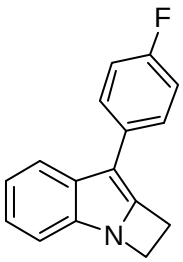
Compound 2d: 40 mg, 86%, A yellow solid, m.p. 62-64 ^{o}C; IR (CH_2Cl_2): ν 2922, 1608, 1437, 1173, 1047, 854, 738 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 2.38 (s, 3H), 3.63 (t, J = 4.4 Hz, 2H), 4.65 (t, J = 4.4 Hz, 2H), 7.14-7.16 (m, 2H), 7.22-7.30 (m, 3H), 7.53 (d, J = 7.6 Hz, 2H), 7.97-7.99 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 21.1, 27.8, 49.9, 109.3, 110.2, 119.9, 120.4, 120.7, 126.6, 129.3, 129.4, 132.2, 134.6, 135.9, 141.2; MS (EI) m/z (%): 233 (95.3) [M^+], 218 (100.0), 204 (10.0), 189 (13.0), 165 (9.4), 149 (20.7), 115 (12.8), 109 (20.2); HRMS (EI) Calcd. for $C_{17}H_{15}N$ (M^+) requires 233.1204, found: 233.1207.



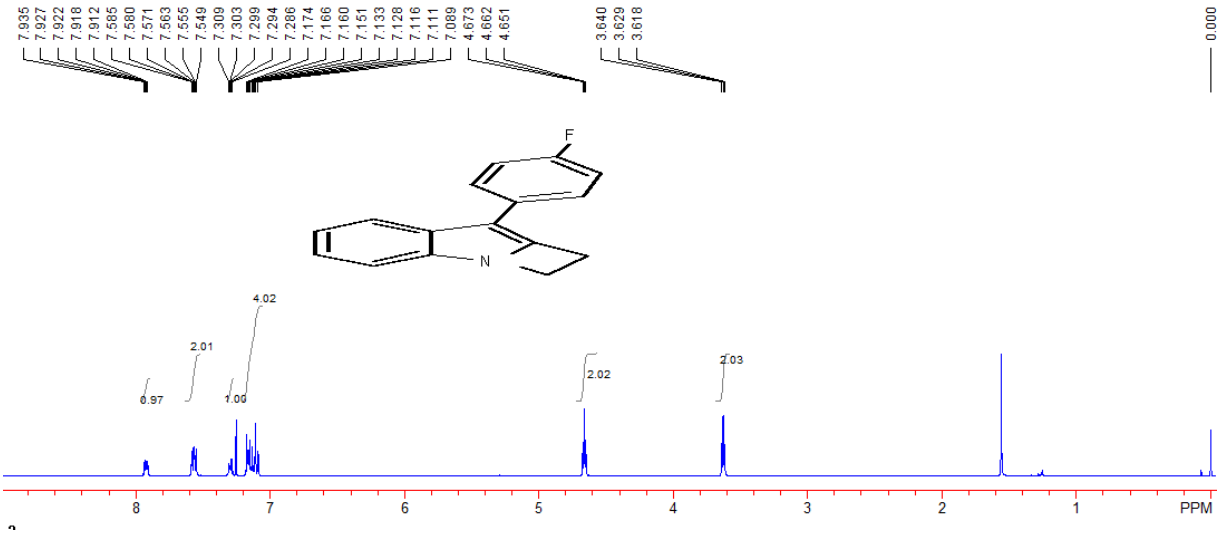


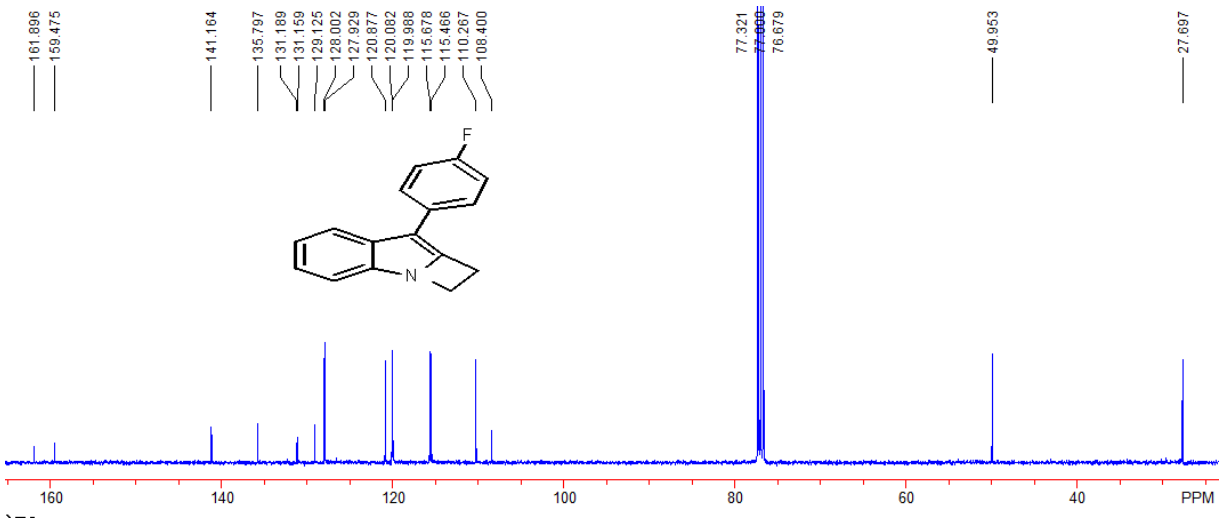
Compound 2e: 39 mg, 78%, A yellow solid, m.p. 121-123 ^{o}C; IR (CH_2Cl_2): ν 3047, 2954, 1607, 1433, 1240, 1031, 825 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 3.61 (t, *J* = 4.4 Hz, 2H), 3.85 (s, 3H), 4.63 (t, *J* = 4.4 Hz, 2H), 6.98 (d, *J* = 8.8 Hz, 2H), 7.13-7.17 (m, 2H), 7.27-7.29 (m, 1H), 7.55 (d, *J* = 8.8 Hz, 2H), 7.93-7.95 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$, TMS): δ 27.7, 49.8, 55.3, 109.1, 110.2, 114.3, 119.8, 120.2, 120.7, 127.78, 127.82, 129.4, 135.9, 140.7, 157.3; MS (ESI) *m/z*: 250.1 (M+H^{+}, 100); HRMS (ESI) Calcd. for $C_{17}H_{16}NO^{+}$ requires: 250.1232, found: 250.1234.

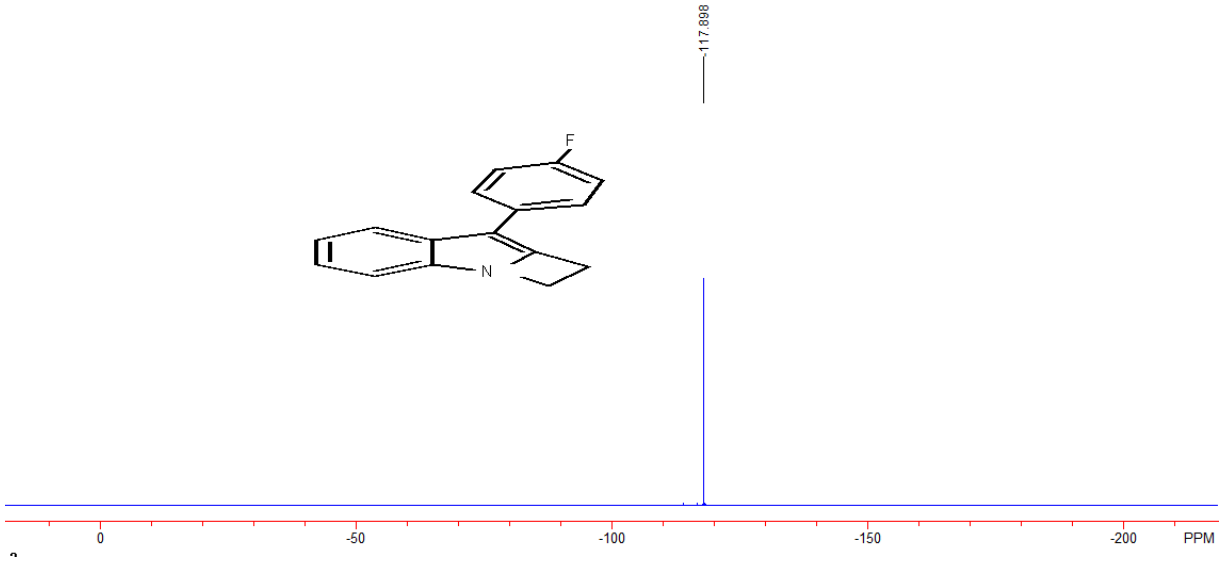


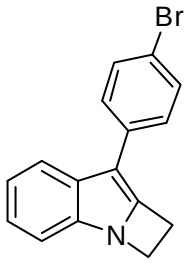


Compound 2f: 39 mg, 82%, A yellow solid, m.p. 111-113 ^{o}C; IR (CH_2Cl_2): ν 3045, 2956, 1607, 1564, 1506, 1437, 1221, 1057, 737 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$, TMS): 3.63 (t, J = 4.4 Hz, 2H), 4.66 (t, J = 4.4 Hz, 2H), 7.09-7.17 (m, 4H), 7.29-7.31 (m, 1H), 7.55-7.59 (m, 2H), 7.91-7.94 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 27.7, 50.0, 108.4, 110.3, 115.6 (d, $J_{C\text{-}F}$ = 21.2 Hz); 120.0, 120.1, 120.9, 128.0 (d, $J_{C\text{-}F}$ = 7.3 Hz), 129.1, 131.2 (d, $J_{C\text{-}F}$ = 3.0 Hz), 135.8, 141.2, 160.7 (d, $J_{C\text{-}F}$ = 242.1 Hz); ^{19}F NMR (376 MHz, $CDCl_3$, $CFCl_3$): δ -117.9 (s); MS (EI) m/z (%): 237 (74.6) [M^+], 236 (100.0), 222 (6.5), 217 (6.4), 207 (7.3), 183 (16.9), 146 (3.4), 118 (12.5); HRMS (EI) Calcd. for $C_{16}H_{12}FN$ (M^+) requires 237.0954, found: 237.0960.

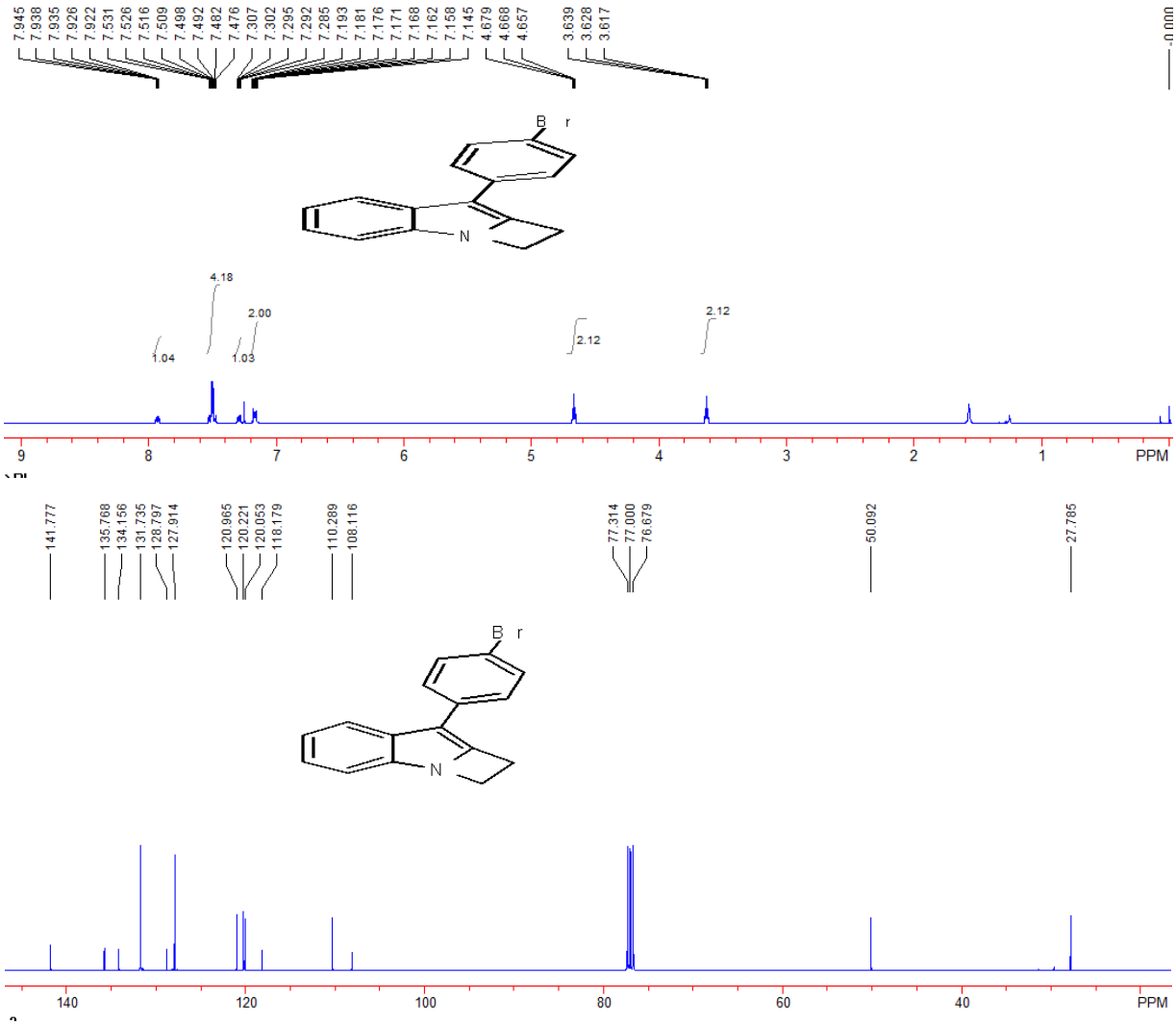


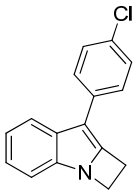




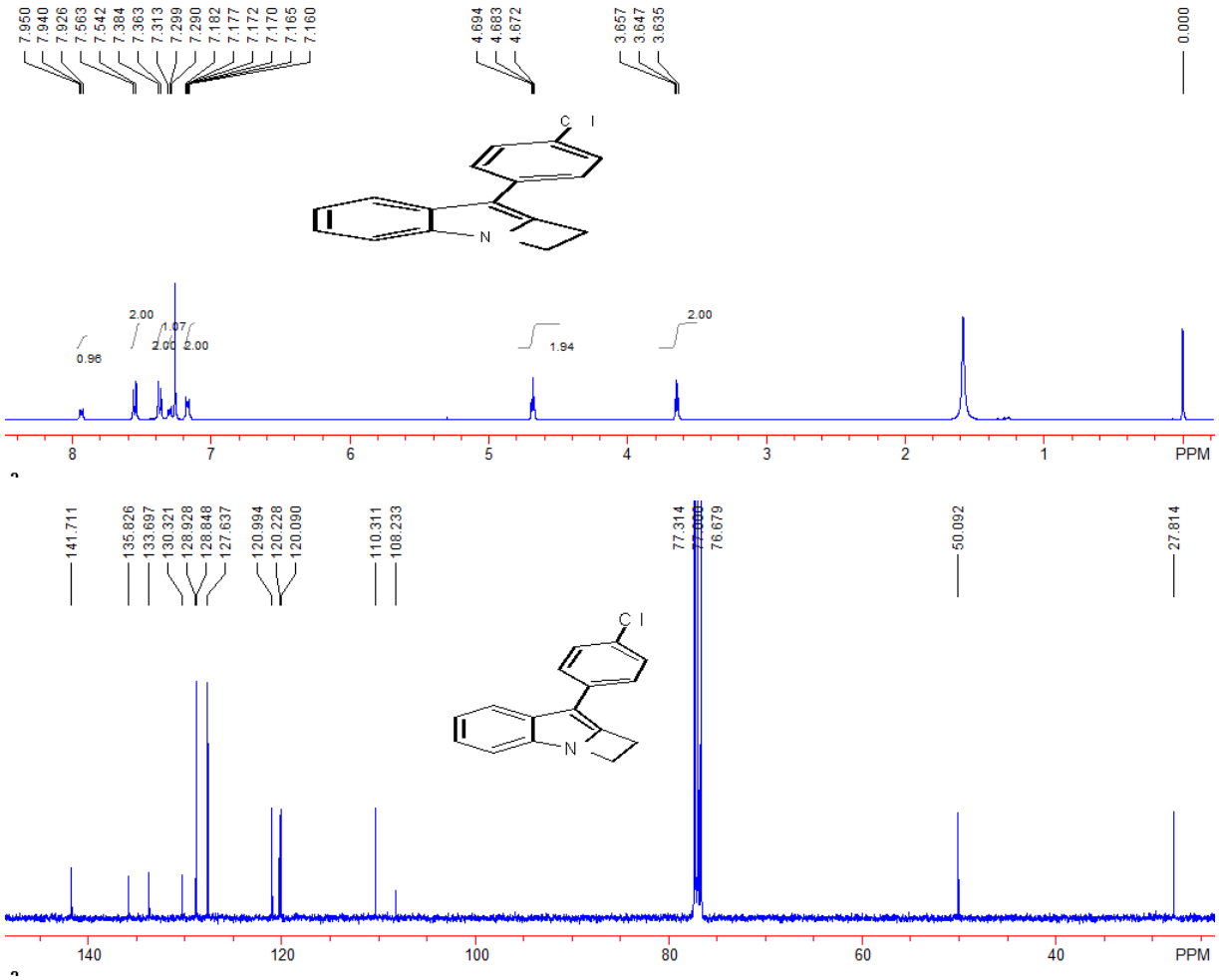


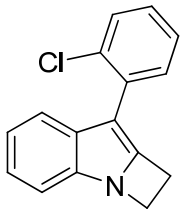
Compound 2g: 48 mg, 81%, A yellow solid, m.p. 99-101 ^{o}C; IR (CH_2Cl_2): ν 3048, 2954, 1560, 1437, 1143, 1046, 738 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$, TMS): 3.63 (t, J = 4.4 Hz, 2H), 4.67 (t, J = 4.4 Hz, 2H), 7.15-7.19 (m, 2H), 7.29-7.31 (m, 1H), 7.48-7.53 (m, 4H), 7.92-7.95 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 27.8, 50.1, 108.1, 110.3, 118.2, 120.1, 120.2, 121.0, 127.9, 128.8, 131.7, 134.2, 135.8, 141.8; MS (EI) m/z (%): 297 (32.2) [M^+], 218 (86.0), 217 (100.0), 203 (4.2), 189 (15.6), 163 (9.7), 109 (24.7), 95 (9.6); HRMS (EI) Calcd. for $C_{16}H_{12}BrN$ (M^+) requires 297.0153, found: 297.0152.



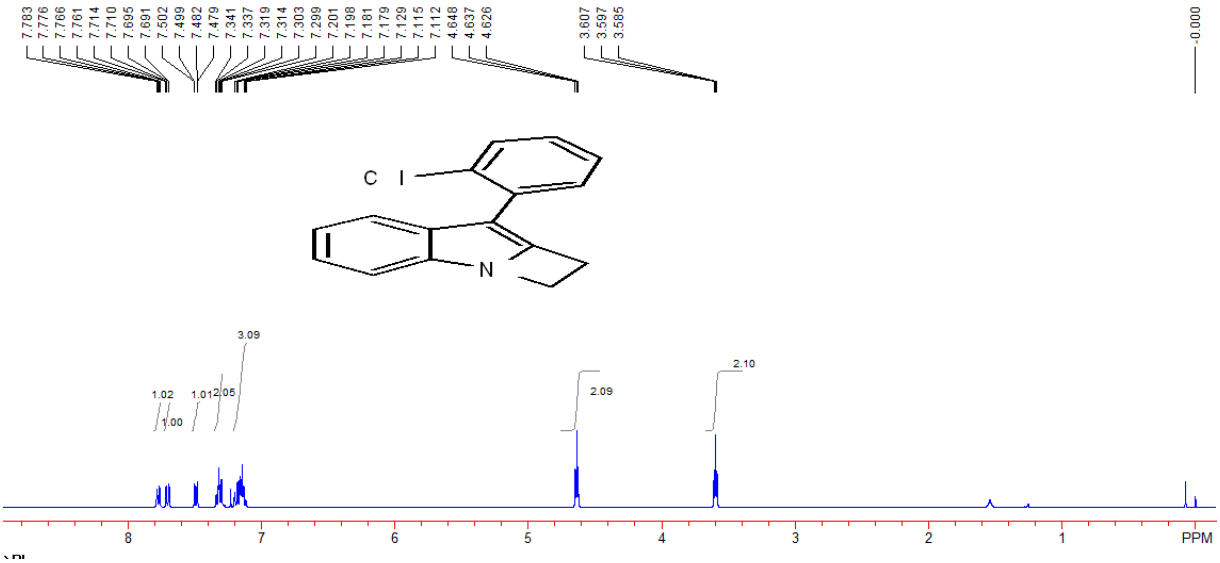


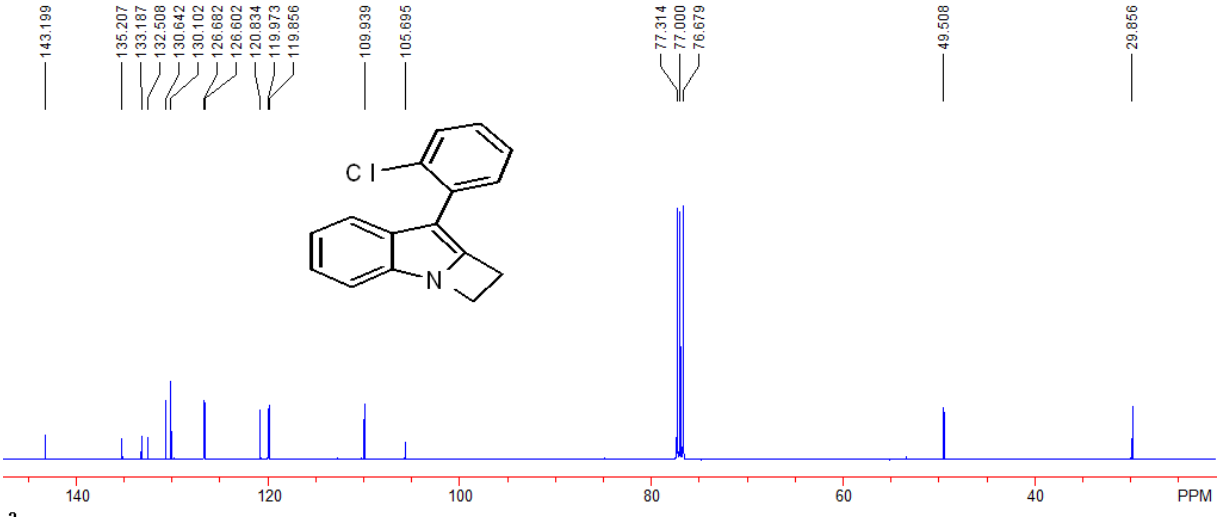
Compound 2h: 42 mg, 83%, A yellow solid, m.p. 94-96 ^{o}C; IR (CH_2Cl_2): ν 2952, 1596, 1491, 1173, 1091, 739 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$, TMS): 3.65 (t, *J* = 4.4 Hz, 2H), 4.68 (t, *J* = 4.4 Hz, 2H), 7.16-7.18 (m, 2H), 7.29-7.31 (m, 1H), 7.37 (d, *J* = 8.4 Hz, 2H), 7.55 (d, *J* = 8.4 Hz, 2H), 7.93-7.95 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 27.8, 50.1, 108.2, 110.3, 120.1, 120.2, 121.0, 127.6, 128.8, 128.9, 130.3, 133.7, 135.8, 141.7; MS (ESI) *m/z*: 254.1 (M+H^{+}, 100); HRMS (ESI) Calcd. for $C_{16}H_{13}ClN^{+}$ requires: 254.0731, found: 254.0736.

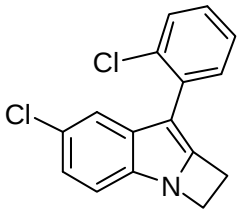




Compound 2i: 40 mg, 79%, A yellow solid, m.p. 85-87 ^{o}C; IR (CH_2Cl_2): ν 3048, 2957, 1593, 1435, 1340, 1037, 740 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$, TMS): 3.60 (t, J = 4.4 Hz, 2H), 4.64 (t, J = 4.4 Hz, 2H), 7.11-7.20 (m, 3H), 7.30-7.34 (m, 2H), 7.49 (dd, J_1 = 8.0 Hz, J_2 = 1.2 Hz, 1H), 7.70 (dd, J_1 = 7.6 Hz, J_2 = 1.6 Hz, 1H), 7.77 (dd, J_1 = 6.4 Hz, J_2 = 2.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 29.9, 49.5, 105.7, 109.9, 119.9, 120.0, 120.8, 126.6, 126.7, 130.1, 130.6, 132.5, 133.2, 135.2, 143.2; MS (ESI) *m/z*: 254.1 ($M+H^+$, 100); HRMS (ESI) Calcd. for $C_{16}H_{13}ClN^+$ requires: 254.0731, found: 254.0734.

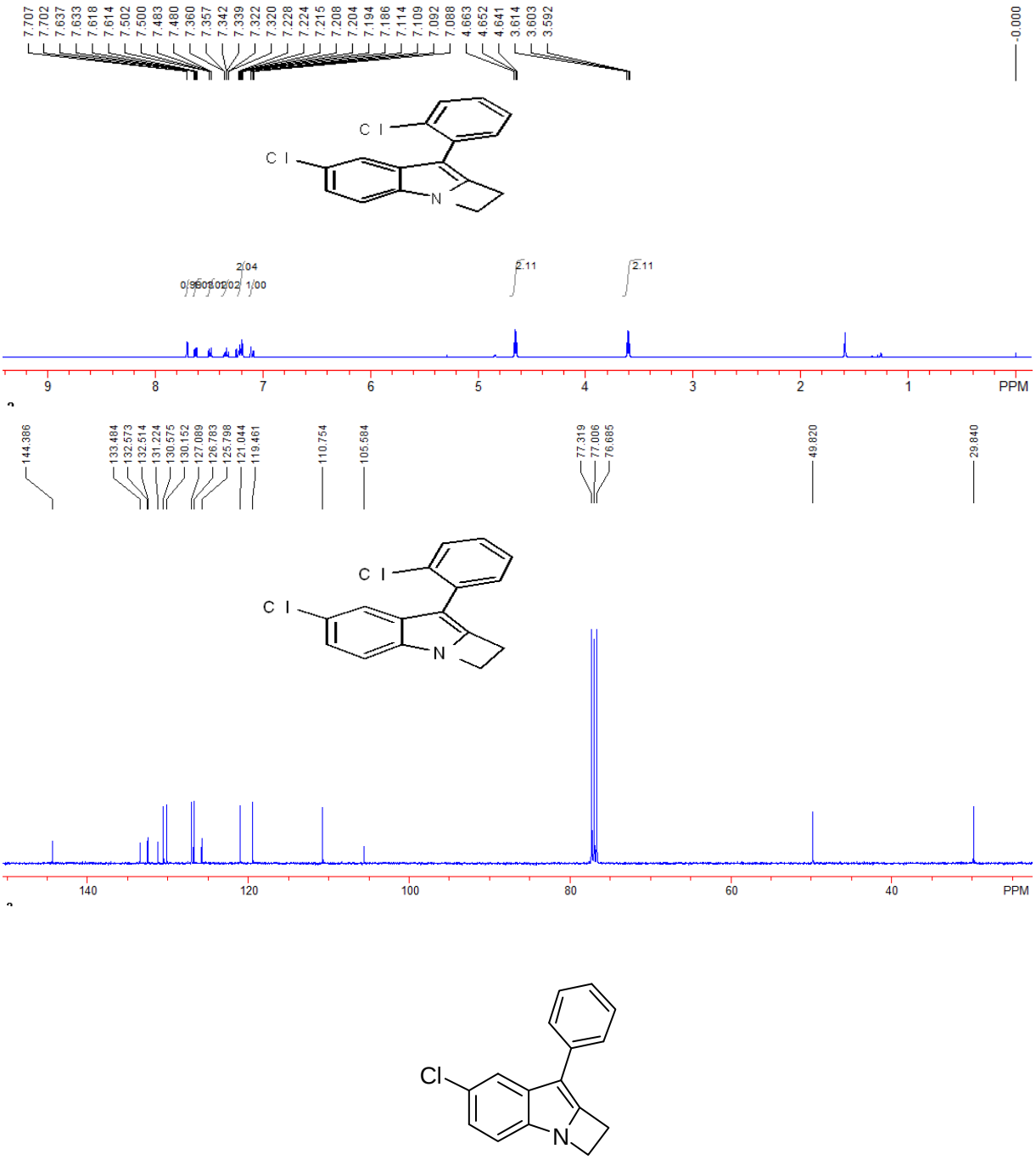






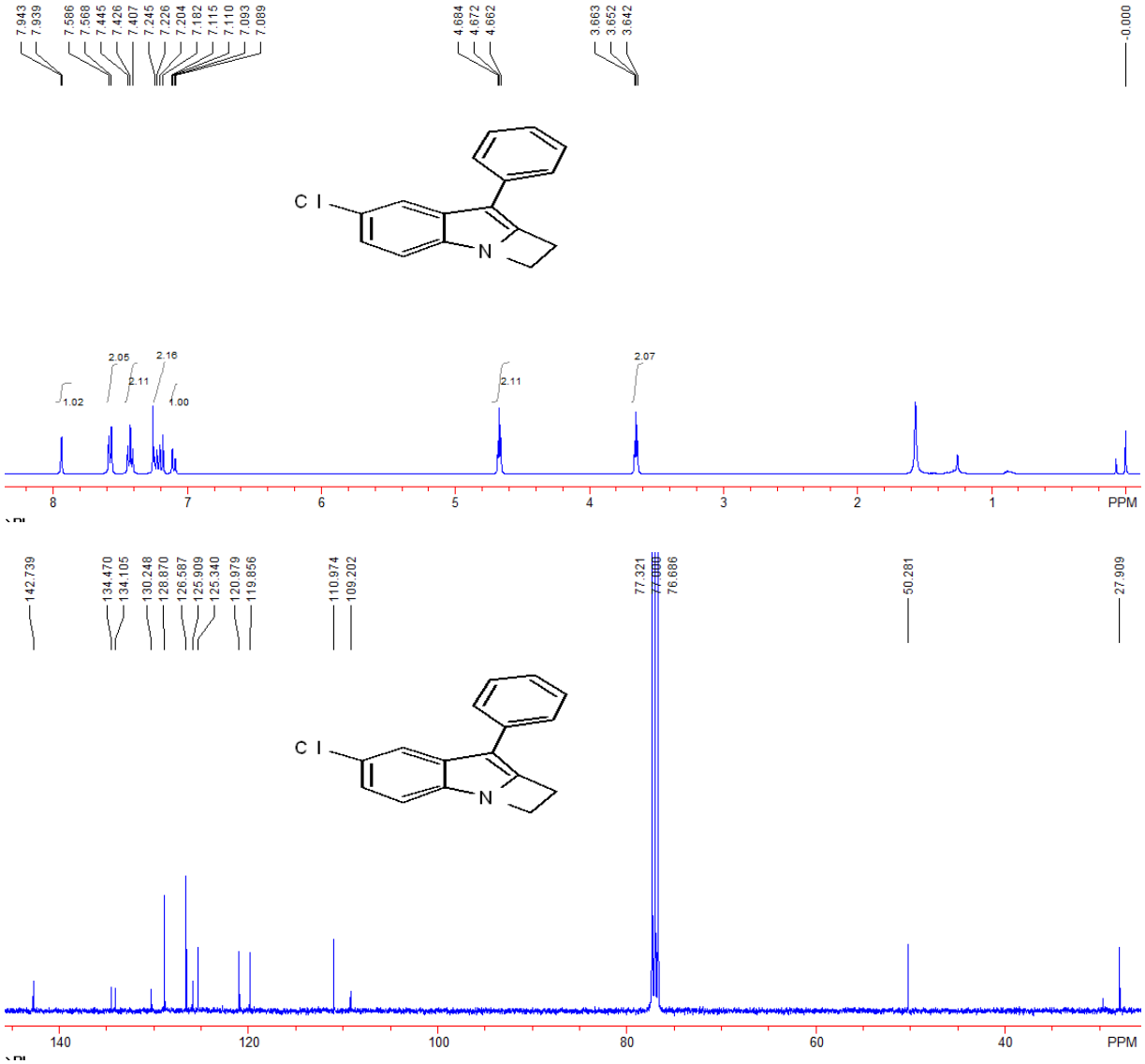
Compound 2j: 44 mg, 77%, A yellow solid, m.p. 88-90 ^{o}C; IR (CH_2Cl_2): ν 3065, 2958, 1611, 1593, 1436, 1036, 788, 759 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$, TMS): 3.60 (t, J = 4.4 Hz, 2H), 4.65 (t, J = 4.4 Hz, 2H), 7.10 (dd, J_1 = 8.8 Hz, J_2 = 2.0 Hz, 1H), 7.19-7.23 (m, 2H), 7.32-7.36 (m, 1H), 7.49 (dd, J_1 = 8.0 Hz, J_2 = 1.2 Hz, 1H), 7.63 (dd, J_1 = 7.6 Hz, J_2 = 2.0 Hz, 1H), 7.70 (d, J = 2.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 29.8, 49.8, 105.6, 110.8, 119.5, 121.0, 125.8, 126.8, 127.1, 130.2, 130.6, 131.2, 132.5, 132.6, 133.5, 144.4; MS (EI) m/z (%): 287 (46.2) [M^{+}],

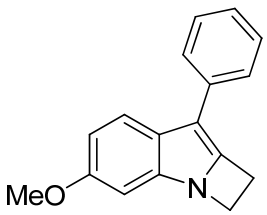
252 (72.2), 217 (100.0), 189 (19.3), 163 (9.9), 126 (9.5), 109 (15.0), 95 (13.2); HRMS (EI) Calcd. for $C_{16}H_{11}Cl_2N$ (M^+) requires 287.0269, found: 287.0268.



Compound 2k: 42 mg, 83%, A yellow solid, m.p. 126-128 ^oC; IR (CH_2Cl_2): ν 3059, 2922, 1602, 1437, 1344, 1066, 763, 698 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$, TMS): 3.65 (t, J = 4.4 Hz, 2H), 4.67 (t, J = 4.4 Hz, 2H), 7.10 (dd, J_1 = 8.8 Hz, J_2 = 2.0 Hz, 1H), 7.18-7.25 (m, 2H), 7.43 (dd, J_1 = J_2 = 7.6 Hz, 2H), 7.58 (d, J = 7.2 Hz, 2H), 7.94 (d, J = 1.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 27.9, 50.3, 109.2, 111.0, 119.9, 121.0, 125.3, 125.9, 126.6, 128.9, 130.2, 134.1, 134.5, 142.7; MS (EI) m/z (%): 253 (77.2) [M^+], 252 (64.2), 218 (58.9), 217 (100.0), 189 (16.4),

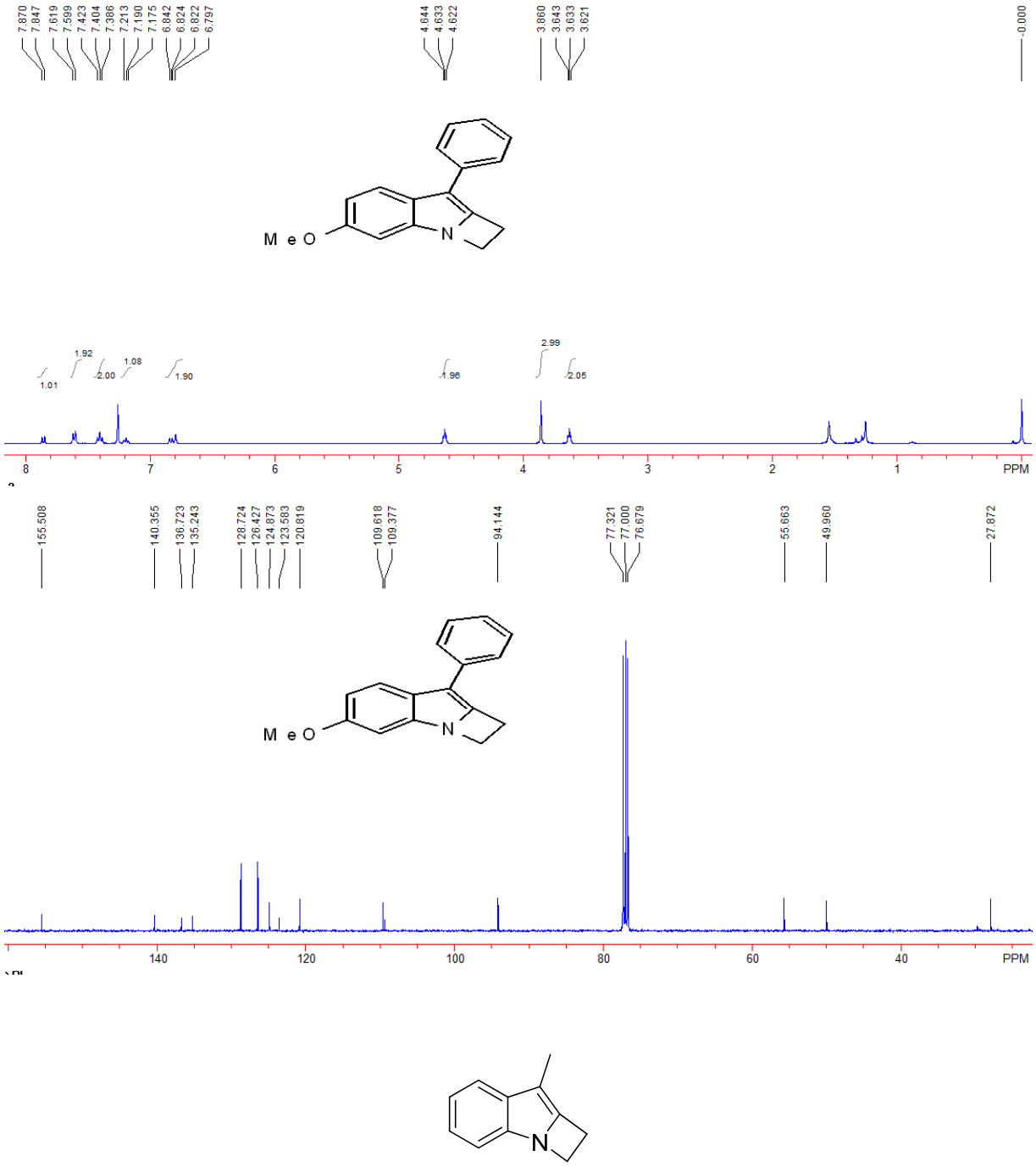
163 (10.1), 109 (25.4), 95 (10.2); HRMS (EI) Calcd. for $C_{16}H_{12}ClN$ (M^+) requires 253.0658, found: 253.0659.



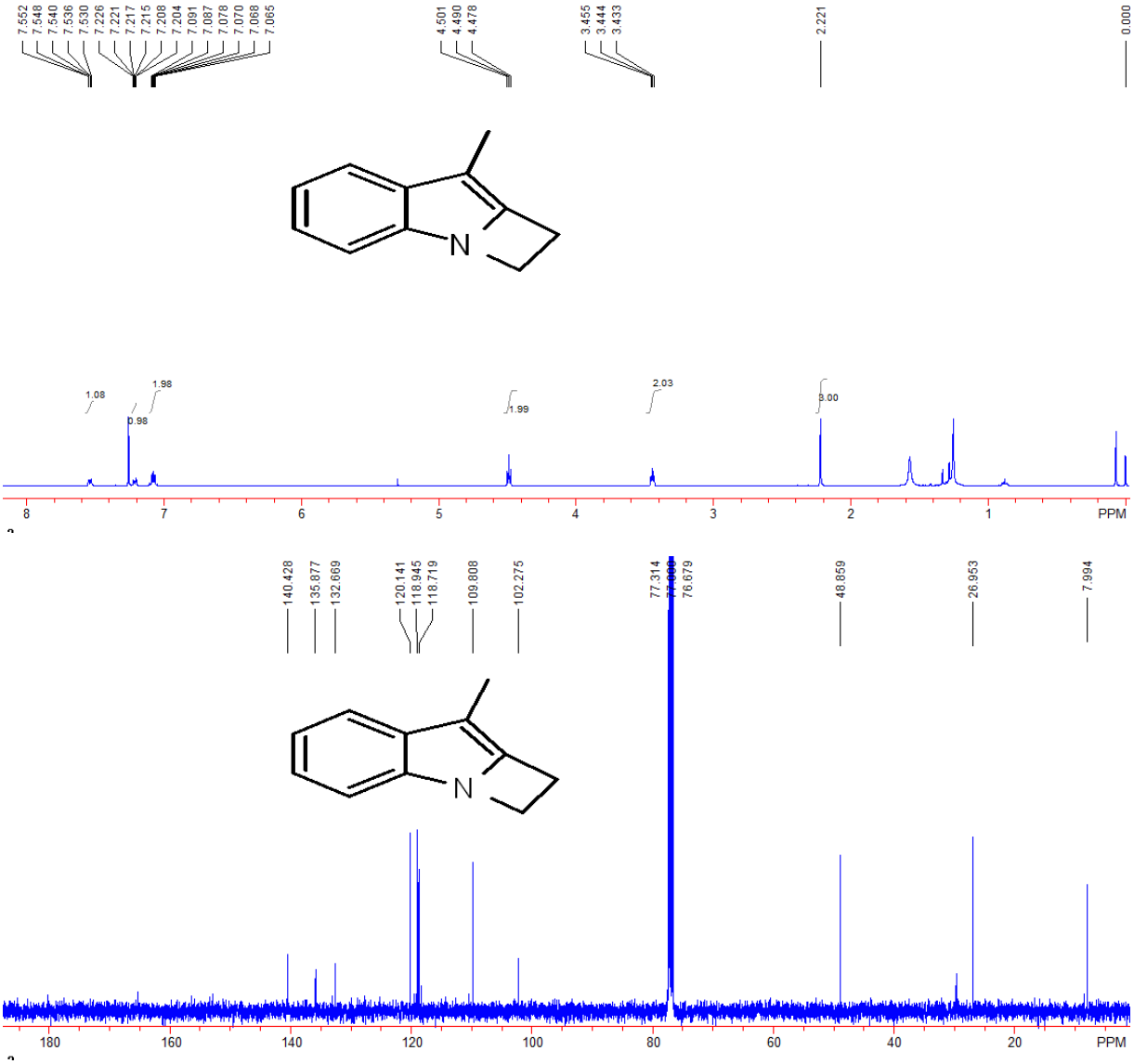


Compound 2l: 36 mg, 72%, A yellow solid, m.p. 106-108 ^{o}C; IR (CH_2Cl_2): ν 2923, 1602, 1486, 1223, 1049, 811, 695 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 3.63 (t, J = 4.4 Hz, 2H), 3.86 (s, 3H), 4.63 (t, J = 4.4 Hz, 2H), 6.80-6.84 (m, 2H), 7.18-7.21 (m, 1H), 7.40 (dd, J_1 = J_2 = 7.6 Hz, 2H), 7.61 (d, J = 8.0 Hz, 2H), 7.86 (d, J = 9.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 27.9, 50.0, 55.7, 94.1, 109.4, 109.6, 120.8, 123.6, 124.9, 126.4, 128.7, 135.2, 136.7, 140.4, 155.5;

MS (ESI) *m/z*: 250.1 ($M+H^+$, 100); HRMS (ESI) Calcd. for $C_{17}H_{16}NO^+$ requires: 250.1226, found: 250.1229.



Compound 2m: 13 mg, 42%, A colorless liquid; IR (CH_2Cl_2): ν 2924, 2853, 1709, 1601, 1484, 1263, 1088, 752 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$, TMS): δ 2.22 (s, 3H), 3.44 (t, J = 4.4 Hz, 2H), 4.90 (t, J = 4.4 Hz, 2H), 7.07-7.09 (m, 2H), 7.20-7.23 (m, 1H), 7.53-7.55 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 8.0, 27.0, 48.9, 102.3, 109.8, 118.7, 118.9, 120.1, 132.7, 135.9, 140.4; MS (EI) m/z (%): 157 (5.2) [M^+], 156 (7.6), 145 (11.1), 144 (100.0), 143 (14.1), 128 (7.0), 115 (7.2), 77 (7.1); HRMS (EI) Calcd. for $C_{11}H_{11}N$ (M^+) requires 157.0891, found: 157.0890.


7.552
7.548
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7.091
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7.078
7.070
7.068
7.065
4.501
4.490
4.478
3.455
3.444
3.433
2.221
0.000
N
1.08
0.98
1.98
1.99
2.03
3.00
PPM
140.428
135.877
132.669
120.141
118.945
118.719
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102.275
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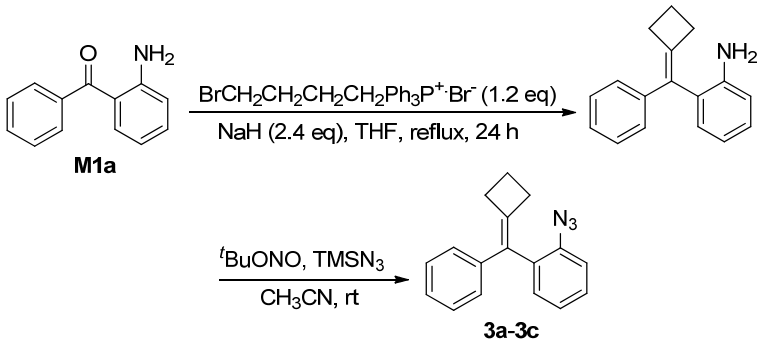
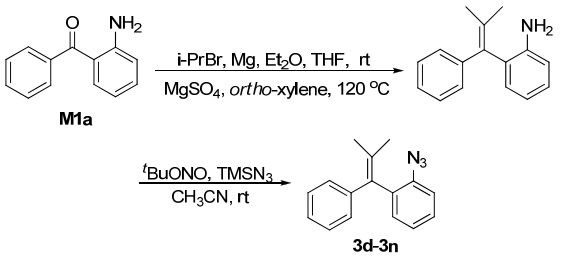
76.679
48.859
26.953
7.994
N
PPM

General procedure for the synthesis of compounds 3



A solution of (4-bromobutyl)triphenylphosphonium bromide (5.7 g, 12 mmol) and NaH (576 mg, 24 mmol) in THF (10 mL) was stirred at 70 ^{o}C for 12 h. Afterwards compound **M1a** (2.0 g 10 mmol) in THF (5 mL) was added and the reaction solution was stirred at 70 ^{o}C for another 12 h. Then the solvent was removed under reduced pressure and the residue was purified by silica gel flash chromatography (eluent: petroleum ether / ethyl acetate = 50 / 1) to afford the product in moderate yield.

To a solution of **S3** (1.0 mmol) in CH_3CN (5 mL) were added ^{t}BuONO (178 μL, 1.5 mmol) and $TMSN_3$ (262 μL, 2.0 mmol), then the resulting reaction mixture was stirred at room temperature for 4 h. The solvent was removed under reduced pressure and the residue was purified by silica gel flash chromatography (eluent: petroleum ether / ethyl acetate = 50 / 1) to afford the product **3** in moderate yield.

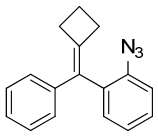


A Grignard reagent was prepared from 2-bromopropane (4.7 mL, 50 mmol) and magnesium (1.3 g, 54mmol) in dry ether (60 mL). The solution of 2-propylmagnesium bromide was added dropwise to a solution of **M1a** (2.0 g 10 mmol) in THF (15 mL) and the mixture was stirred at room temperature overnight. The resulting mixture was quenched by saturated aqueous NH_4Cl

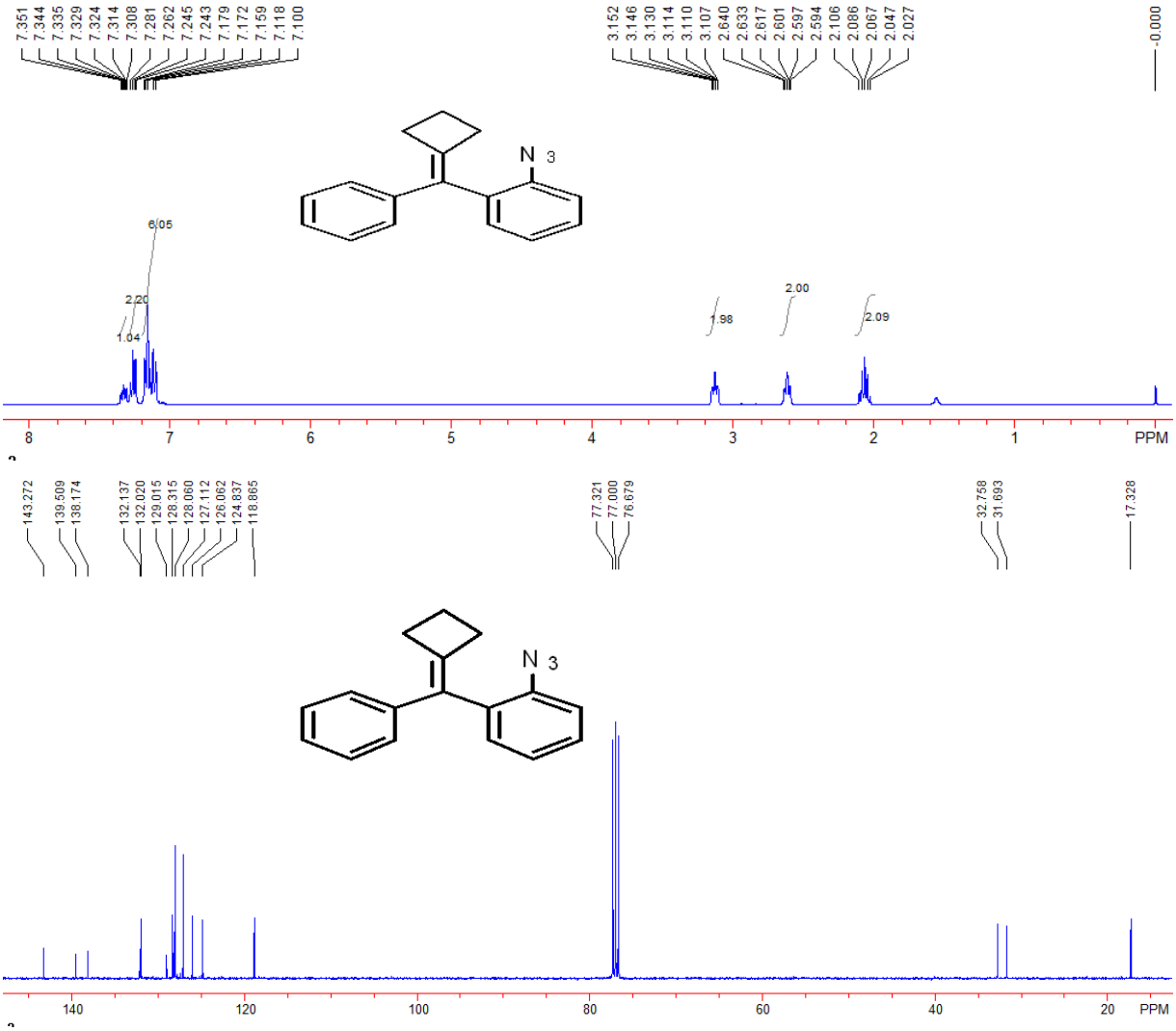
(10 mL), extracted with EtOAc (10 mL x 3), and washed by brine (10 mL). The combined extracts were dried over Na_2SO_4. Then the solvent was removed under reduced pressure to get the crude product without purification. The crude product and $MgSO_4$ (6.0 g, 50 mmol) were combined in *ortho*-xylene (20 mL) and the mixture was heated at 120 ^oC overnight. Then the solvent was removed under reduced pressure and the residue was purified by silica gel flash chromatography (eluent: petroleum ether / ethyl acetate = 50 / 1) to afford the product in good yield.

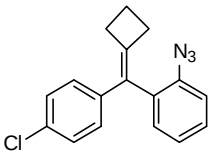
To a solution of **S3** (1.0 mmol) in CH_3CN (5.0 mL) were added ^tBuONO (178 μL, 1.5 mmol) and $TMSN_3$ (262 μL, 2.0 mmol), then the resulting reaction mixture was stirred at room temperature for 4 h. The solvent was removed under reduced pressure and the residue was purified by silica gel flash chromatography (eluent: petroleum ether / ethyl acetate = 50 / 1) to afford the product **3** in moderate yield.

Spectroscopic data for compounds 3

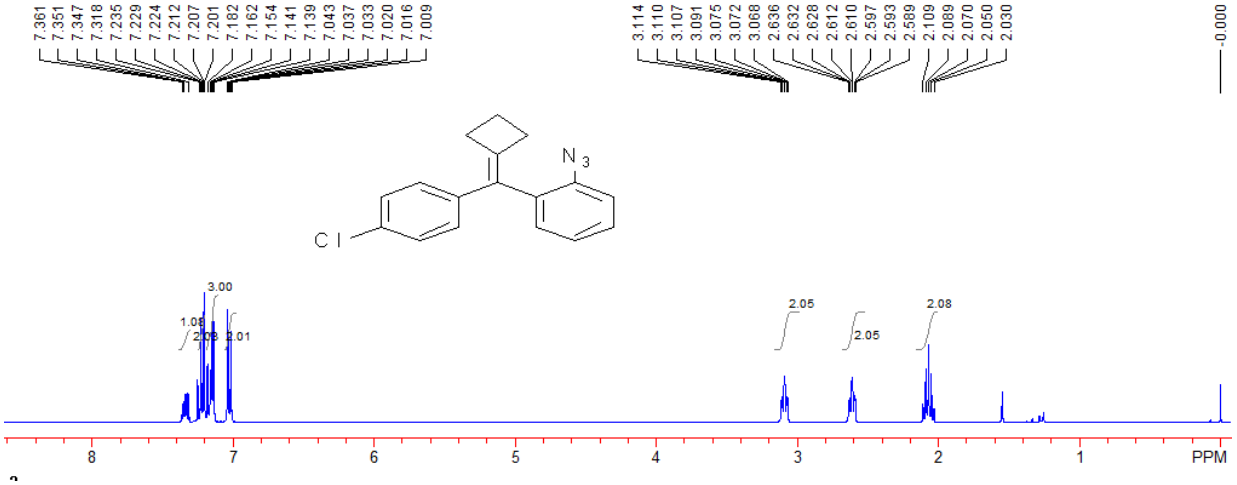


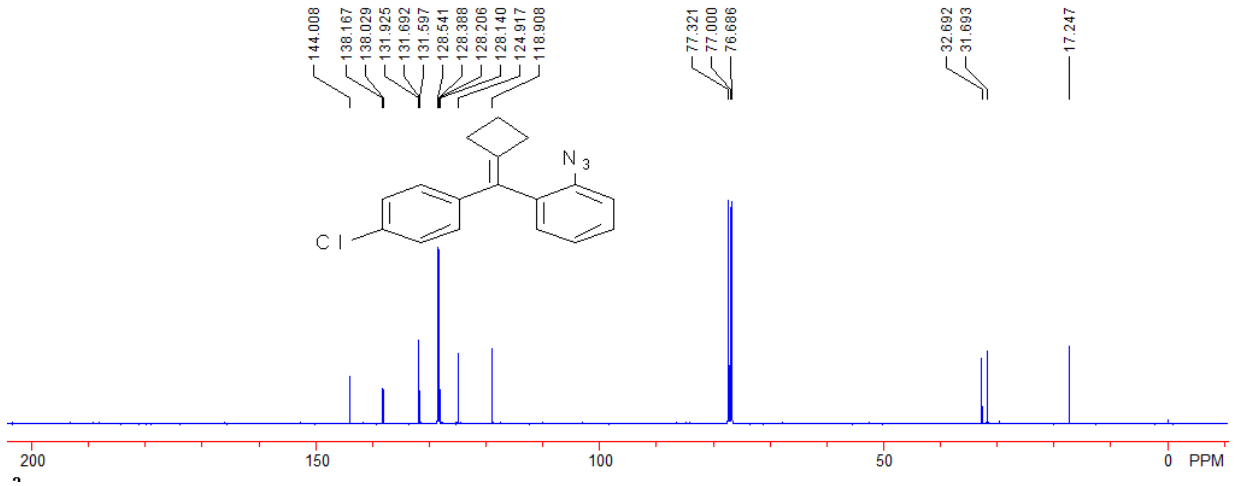
Compound 3a: 104 mg, 40%, A yellow solid, m.p. 106-108 ^{o}C; IR (CH_2Cl_2): ν 3054, 2952, 2122, 2089, 1494, 1287, 753 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 2.03-2.11 (m, 2H), 2.59-2.64 (m, 2H), 3.11-3.15 (m, 2H), 7.10-7.18 (m, 6H), 7.24-7.28 (m, 2H), 7.31-7.35 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 17.3, 31.7, 32.8, 118.9, 124.8, 126.1, 127.1, 128.1, 128.3, 129.0, 132.0, 132.1, 138.2, 139.5, 143.3; MS (EI) m/z (%): 233 (100.0) [M-N_2^+], 217 (43.9), 204 (97.6), 190 (11.4), 176 (15.9), 165 (15.4), 152 (11.1), 115 (15.1); HRMS (EI) Calcd. for $C_{17}H_{15}N$ (M-N_2^+) requires 233.1204, found: 233.1205.

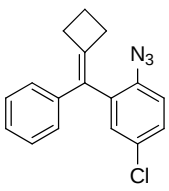




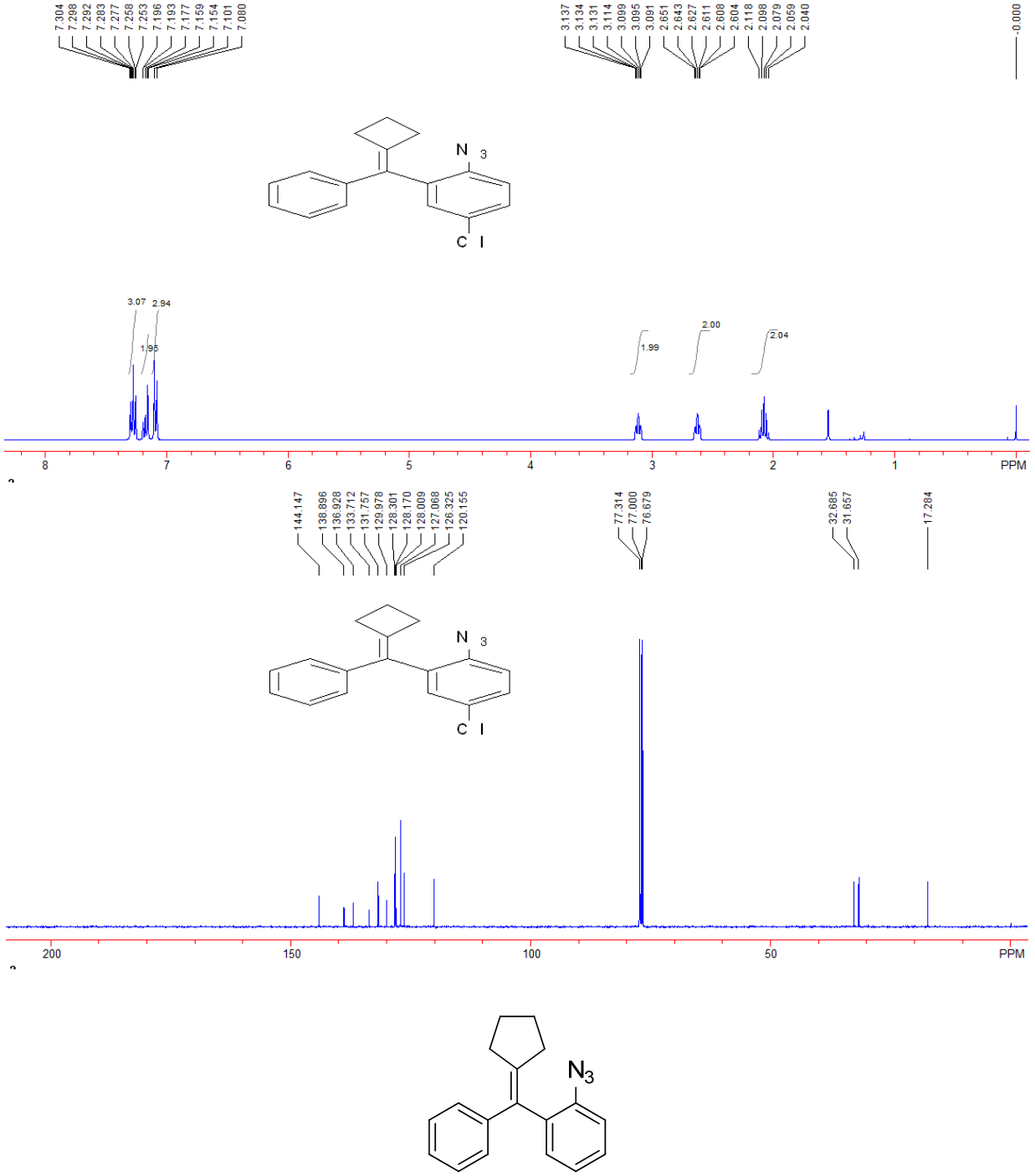
Compound 3b: 200 mg, 68%, A yellow solid, m.p. 116-118 ^{o}C; IR (CH_2Cl_2): ν 2952, 2914, 2124, 2093, 1479, 1298, 768 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 2.03-2.11 (m, 2H), 2.59-2.64 (m, 2H), 3.07-3.11 (m, 2H), 7.01-7.04 (m, 2H), 7.14-7.18 (m, 3H), 7.20-7.24 (m, 2H), 7.32-7.36 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 17.2, 31.7, 32.7, 118.9, 124.9, 128.1, 128.2, 128.4, 128.5, 131.6, 131.7, 131.9, 138.0, 138.2, 144.0; MS (EI) m/z (%): 267 (100,0) [M-N_2^+], 268 (43.1), 266 (77.7), 238 (29.8), 231 (33.7), 217 (38.1), 204 (90.6), 203 (46.1); HRMS (EI) Calcd. for $C_{17}H_{14}NCl$ (M-N_2^+) requires 267.0815, found: 267.0819.



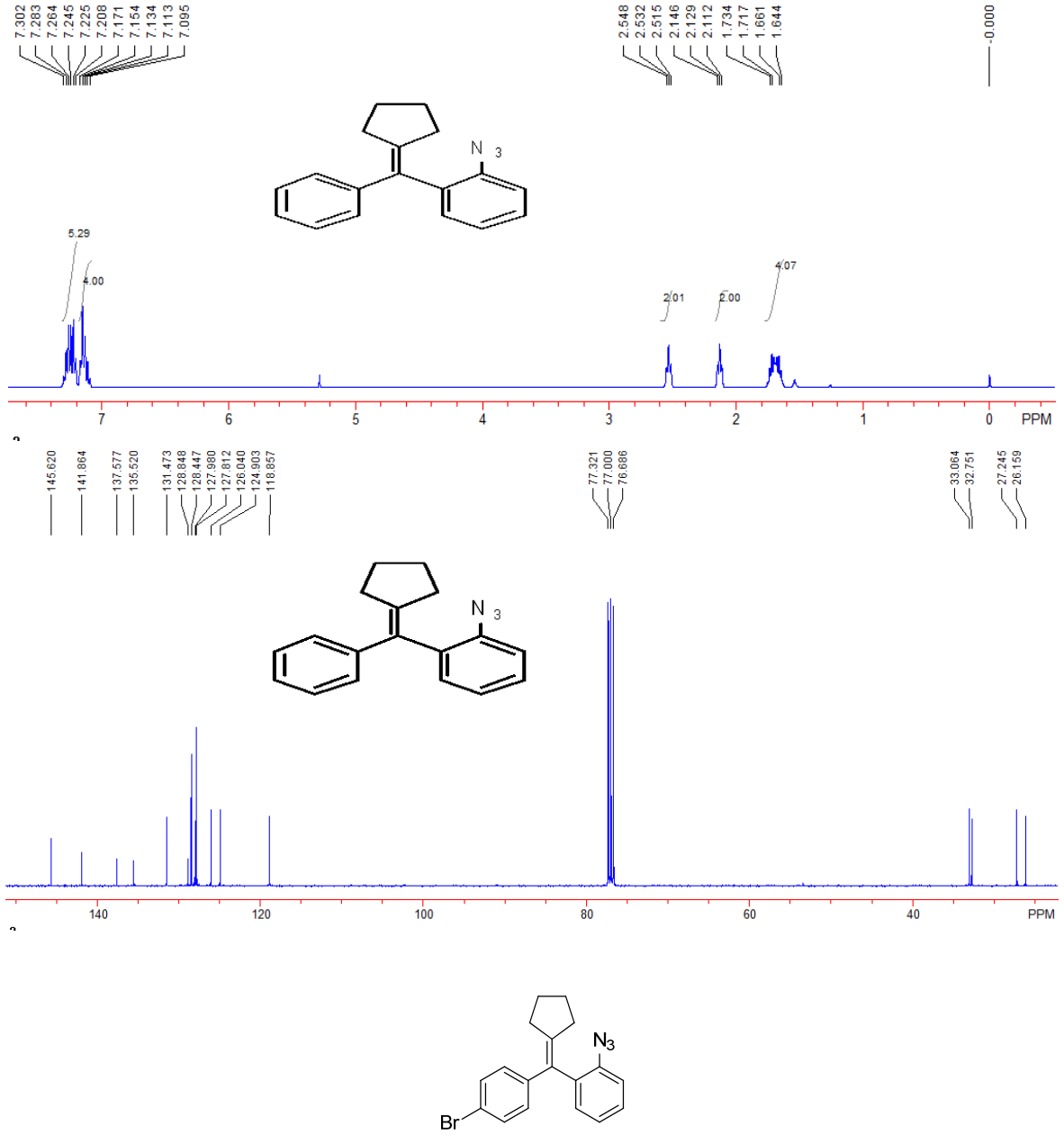




Compound 3c: 153 mg, 52%, A yellow solid, m.p. 96-98 ^{o}C; IR (CH_2Cl_2): ν 2952, 2915, 2121, 2089, 1490, 1293, 752 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 2.04-2.12 (m, 2H), 2.60-2.65 (m, 2H), 3.09-3.14 (m, 2H), 7.09 (d, J = 8.4 Hz, 3H), 7.15-7.20 (m, 2H), 7.25-7.30 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 17.3, 31.7, 32.7, 120.2, 126.3, 127.1, 128.0, 128.2, 128.3, 130.0, 131.8, 133.7, 136.9, 138.9, 144.1; MS (EI) m/z (%): 204 (100.0) [M-N_2^+], 267 (97.2), 266 (65.5), 231 (33.4), 230 (30.1), 217 (32.6), 203 (39.1), 176 (20.3); HRMS (EI) Calcd. for $C_{17}H_{14}NCl$ (M-N_2^+) requires 267.0815, found: 267.0809.

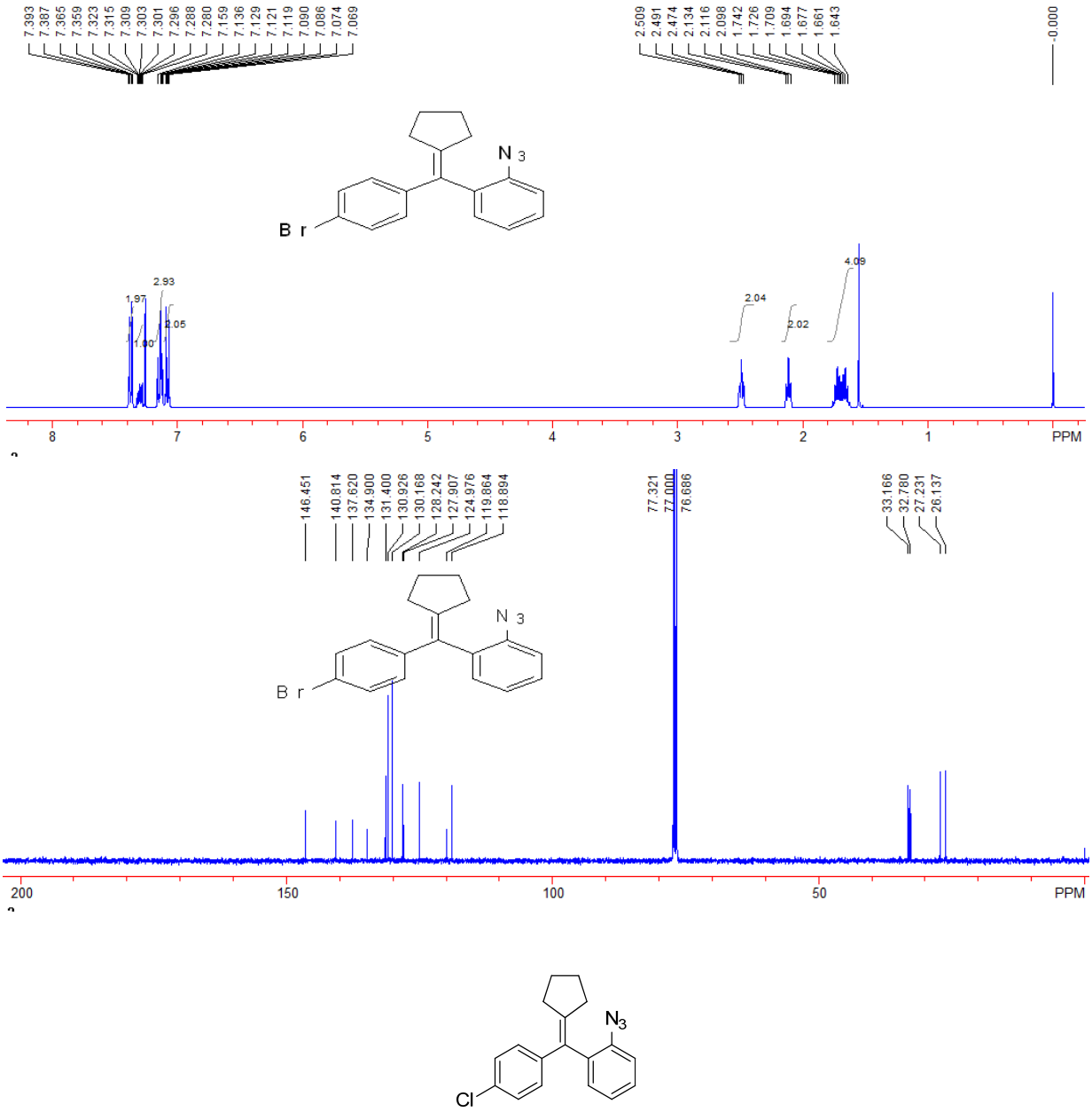


Compound 3d: 212 mg, 77%, A yellow solid, m.p. 82-84 ^{o}C; IR (CH_2Cl_2): ν 2953, 2121, 2092, 1484, 1284, 751, 699 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 1.64-1.73 (m, 4H), 2.13 (t, J = 6.8 Hz, 2H), 2.53 (t, J = 6.8 Hz, 2H), 7.10-7.17 (m, 4H), 7.21-7.30 (m, 5H); ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 26.2, 27.2, 32.8, 33.1, 118.9, 124.9, 126.0, 127.8, 128.0, 128.4, 128.8, 131.5, 135.5, 137.6, 141.9, 145.6; MS (EI) m/z (%): 247 (100.0) [M-N_2^+], 218 (87.4), 204 (32.7), 178 (13.6), 170 (13.0), 165 (14.1), 152 (10.7), 115 (12.4); HRMS (EI) Calcd. for $C_{18}H_{17}N$ (M-N_2^+) requires 247.1361, found: 247.1362.



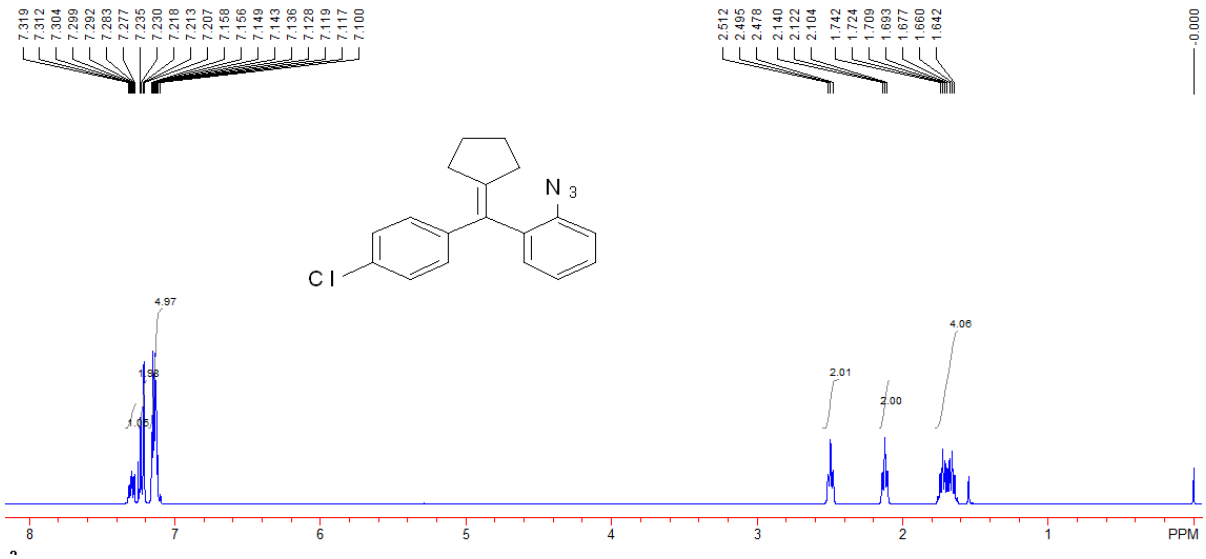
Compound 3e: 292 mg, 83%, A yellow solid, m.p. 112-114 ^{o}C; IR (CH_2Cl_2): ν 2953, 2866, 2119, 2087, 1485, 1287, 751 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 1.64-1.74 (m, 4H), 2.12 (t, J = 7.2 Hz, 2H), 2.49 (t, J = 7.2 Hz, 2H), 7.07-7.09 (m, 2H), 7.12-7.16 (m, 3H), 7.28-7.32 (m, 1H),

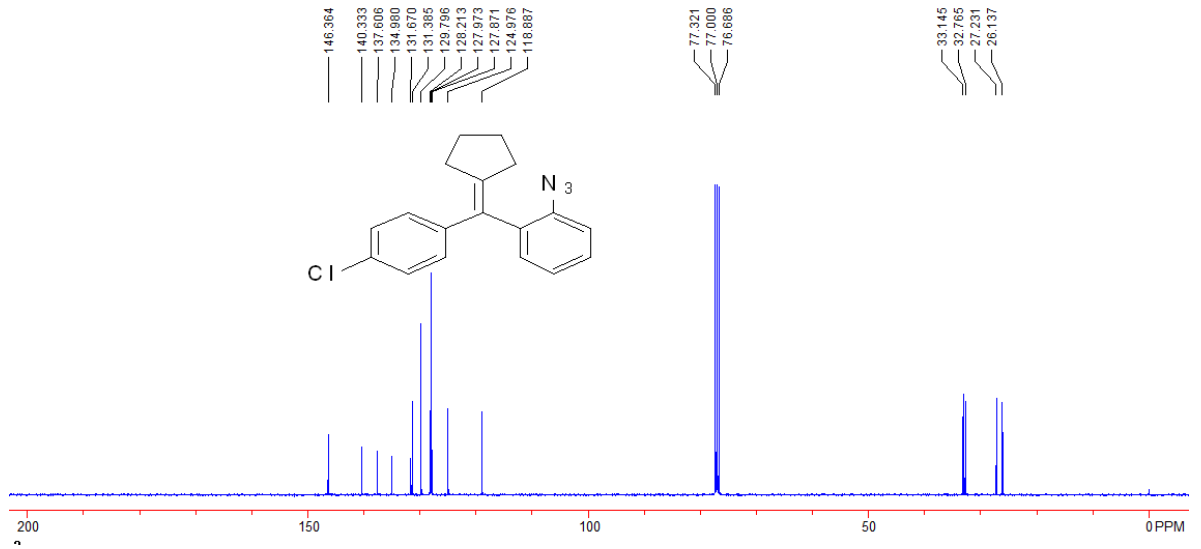
7.36-7.39 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 26.1, 27.2, 32.8, 33.2, 118.9, 119.9, 125.0, 127.9, 128.2, 130.2, 130.9, 131.4, 134.9, 137.6, 140.8, 146.5; MS (EI) m/z (%): 325 (100.0) [M-N_2^+], 327 (94.6), 326 (57.9), 297 (33.8), 246 (21.3), 218 (53.4), 217 (92.2), 204 (45.1); HRMS (EI) Calcd. for $C_{18}H_{16}NBr$ (M-N_2^+) requires 325.0466, found: 325.0468.

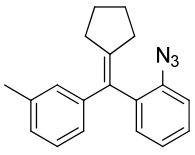


Compound 3f: 256 mg, 82%, A yellow solid, m.p. 92-94 ^{o}C; IR (CH_2Cl_2): ν 2954, 2867, 2120, 2087, 1487, 1291, 751 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 1.64-1.74 (m, 4H), 2.12 (t, *J* = 7.2 Hz, 2H), 2.50 (t, *J* = 7.2 Hz, 2H), 7.10-7.16 (m, 5H), 7.21-7.24 (m, 2H), 7.28-7.32 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 26.1, 27.2, 32.8, 33.1, 118.9, 125.0, 127.9, 128.0, 128.2, 129.8, 131.4, 131.7, 135.0, 137.6, 140.3, 146.4; MS (EI) m/z (%): 281 (100.0) [M-N_2^+], 282

(36.2), 280 (59.6), 253 (42.2), 218 (36.5), 217 (54.5), 204 (30.0), 107 (12.4); HRMS (EI) Calcd. for $C_{18}H_{16}NCl$ ($M-N_2^+$) requires 281.0971, found: 281.0977.

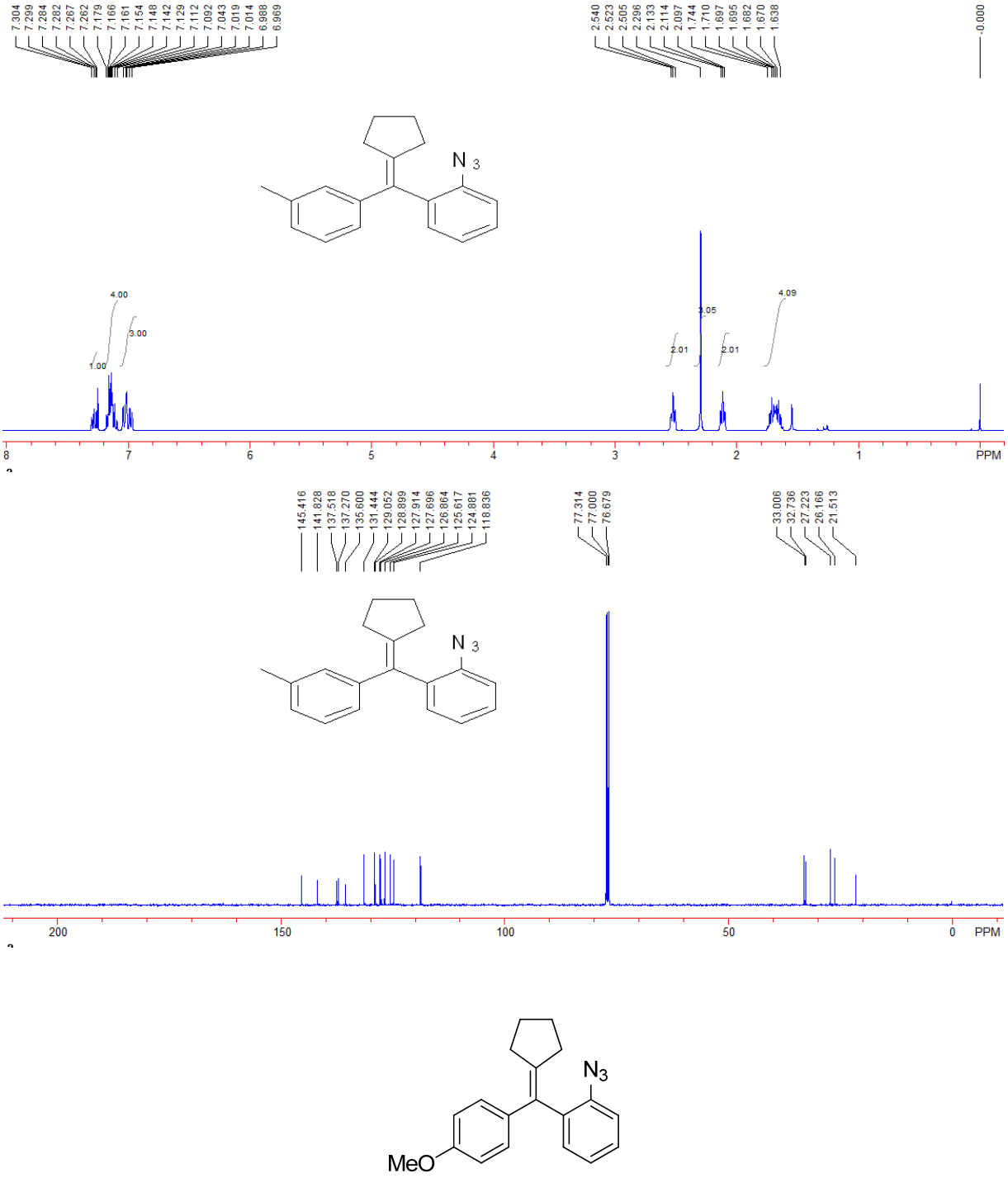






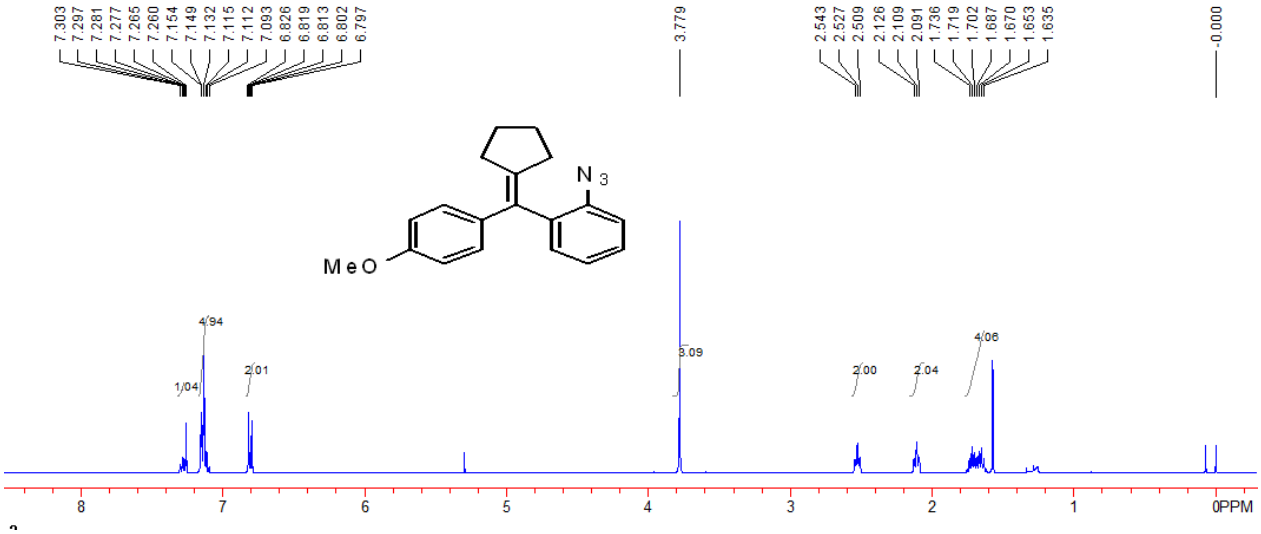
Compound 3g: 249 mg, 86%, A yellow solid, m.p. 74-76 ^{o}C; IR (CH_2Cl_2): ν 2953, 2866, 2119, 2089, 1483, 1296, 751 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 1.64-1.74 (m, 4H), 2.11 (t, J = 7.2 Hz, 2H), 2.30 (s, 3H), 2.52 (t, J = 7.2 Hz, 2H), 6.97-7.04 (m, 3H), 7.09-7.18 (m, 4H), 7.26-7.30 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 21.5, 26.2, 27.2, 32.7, 33.0, 118.8, 124.9, 125.6, 126.9, 127.7, 127.9, 128.9, 129.1, 131.4, 135.6, 137.3, 137.5, 141.8, 145.4; MS (EI)

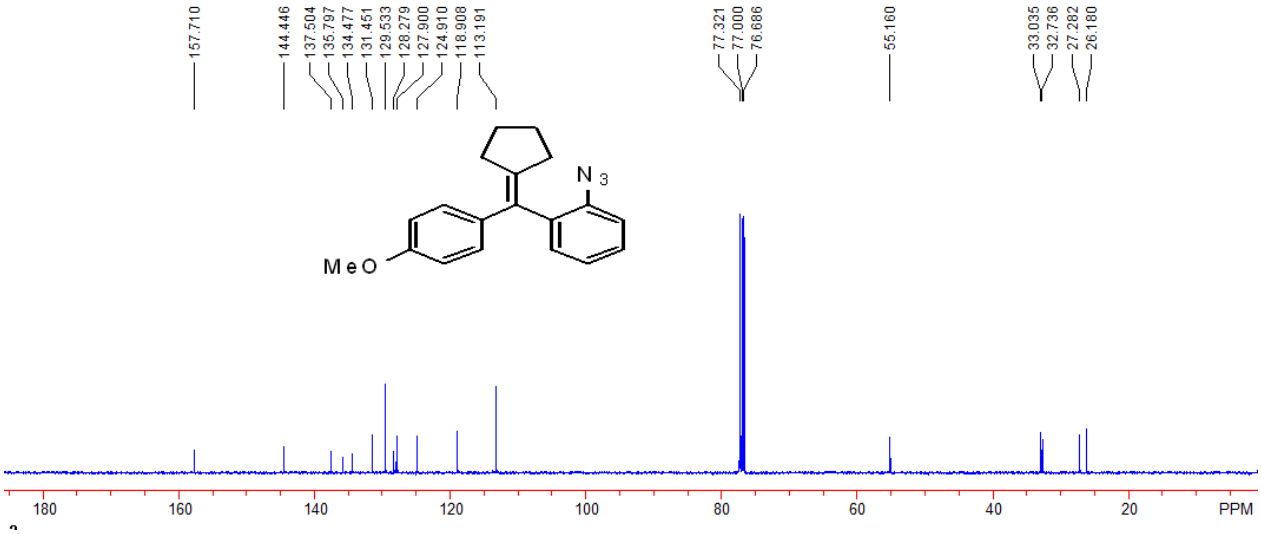
m/z (%): 261 (100.0) [M-N_2^+], 260 (57.4), 233 (35.0), 323 (39.0), 218 (33.0), 217 (34.1), 204 (17.7), 178 (7.9); HRMS (EI) Calcd. for $C_{19}H_{19}N$ (M-N_2^+) requires 261.1517, found: 261.1515.

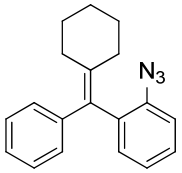


Compound 3h: 190 mg, 63%, A yellow solid, m.p. 111-113 ^oC; IR (CH_2Cl_2): ν 2953, 2866, 2121, 2089, 1510, 1284, 1246, 831 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$, TMS): δ 1.64-1.74 (m, 4H), 2.11 (t, J = 7.2 Hz, 2H), 2.53 (t, J = 7.2 Hz, 2H), 6.80-6.83 (m, 2H), 7.09-7.15 (m, 5H), 7.26-7.30 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 26.2, 27.3, 32.7, 33.0, 55.2, 113.2, 118.9, 124.9,

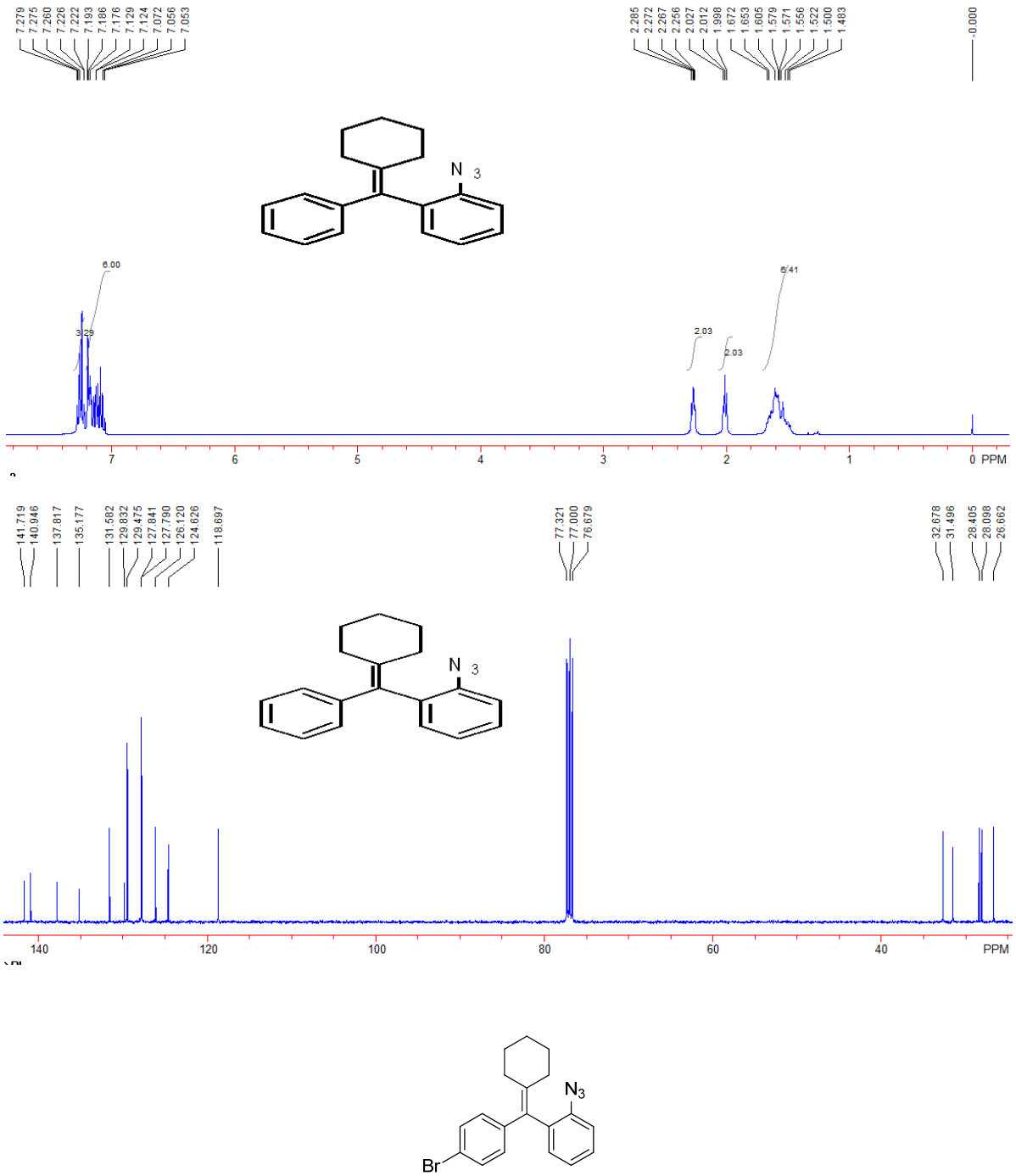
127.9, 128.3, 129.5, 131.5, 134.5, 135.8, 137.5, 144.4, 157.7; MS (ESI) *m/z*: 306.2 ($M+H^+$, 100); HRMS (ESI) Calcd. for $C_{19}H_{20}N_3O^+$ requires: 306.1606, found: 306.1613.



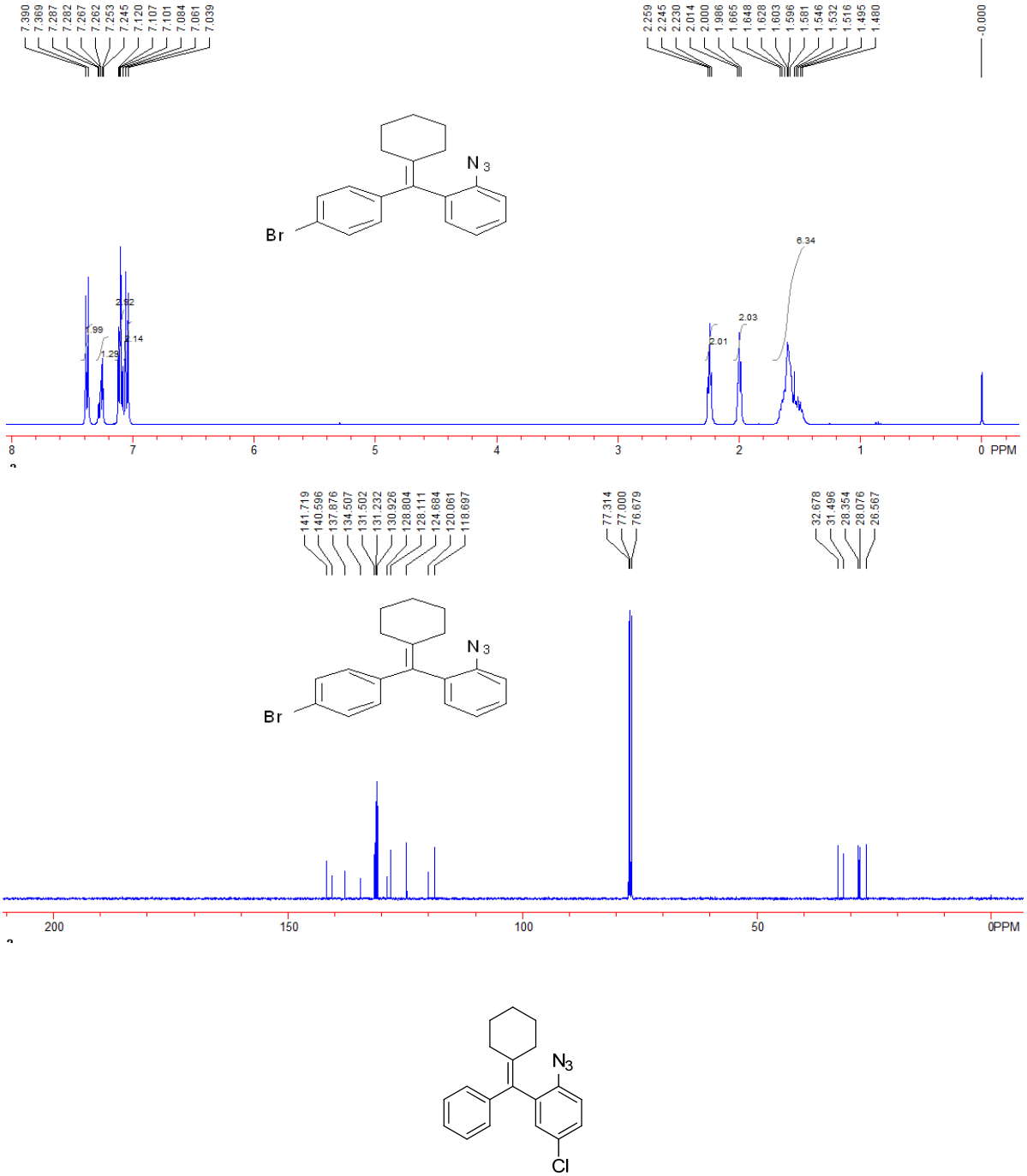




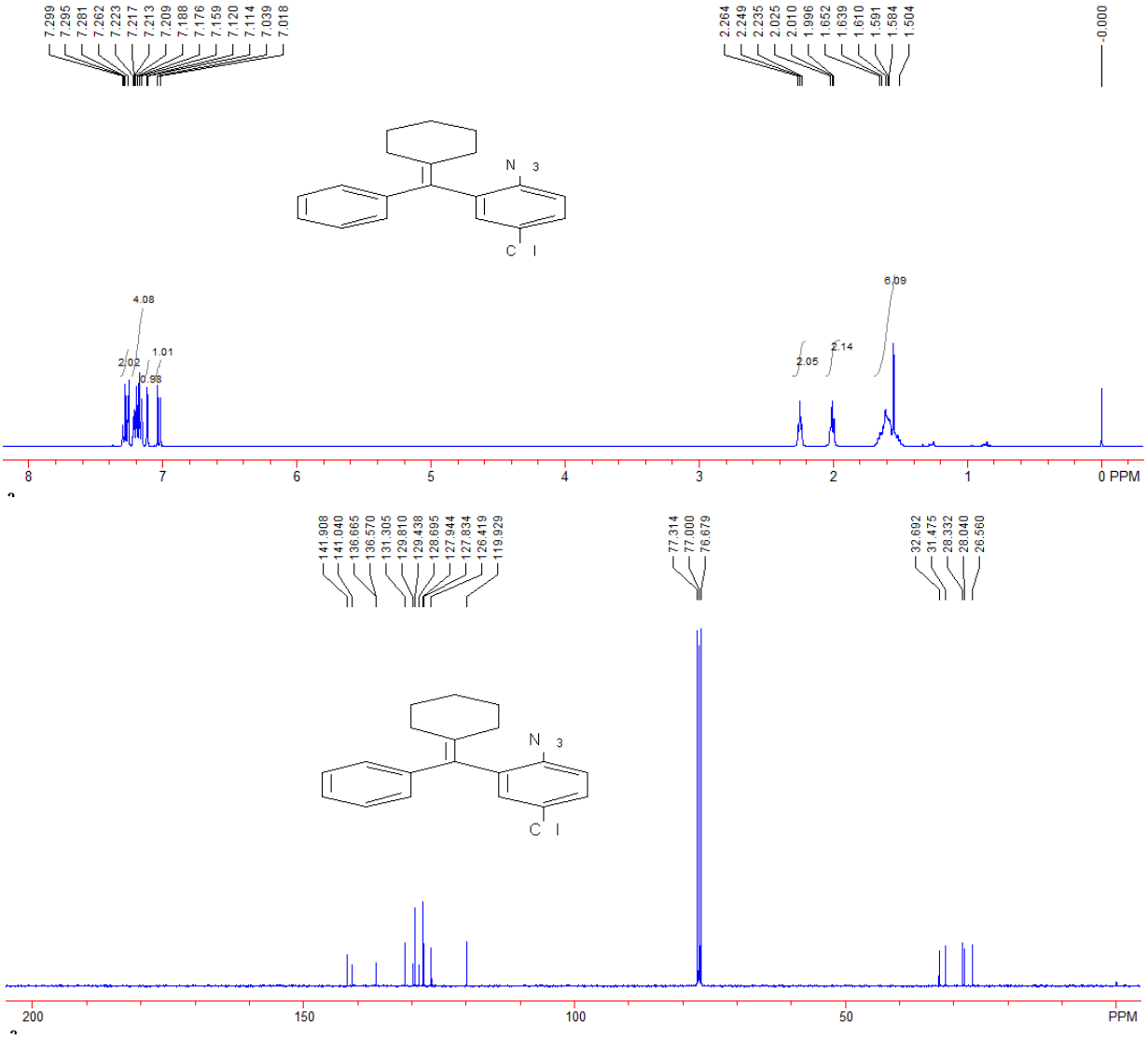
Compound 3i: 214 mg, 74%, A yellow solid, m.p. 74-76 ^oC; IR (CH_2Cl_2): ν 2925, 2852, 2120, 2085, 1484, 1289, 751 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$, TMS): δ 1.48-1.67 (m, 6H), 2.01 (t, J = 5.6 Hz, 2H), 2.26-2.29 (m, 2H), 7.05-7.23 (m, 6H), 7.26-7.28 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 26.7, 28.1, 28.4, 31.5, 32.7, 118.7, 124.6, 126.1, 127.8, 129.5, 129.8, 131.6, 135.2, 137.8, 140.9, 141.7; MS (EI) m/z (%): 261 (100.0) [$M-N_2^+$], 246 (11.6), 232 (61.2), 218 (36.6), 204 (47.9), 178 (20.3), 165 (20.8), 115 (15.3); HRMS (EI) Calcd. for $C_{19}H_{19}N$ ($M-N_2^+$) requires 261.1517, found: 261.1520.

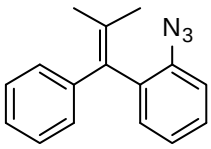


Compound 3j: 286 mg, 78%, A yellow solid, m.p. 91-93 ^{o}C; IR (CH_2Cl_2): ν 2926, 2852, 2119, 2084, 1483, 1290, 750 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 1.48-1.67 (m, 6H), 2.00 (t, J = 5.6 Hz, 2H), 2.25 (t, J = 5.6 Hz, 2H), 7.05 (d, J = 8.8 Hz, 2H), 7.08-7.12 (m, 3H), 7.25-7.29 (m, 1H), 7.38 (d, J = 8.4 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 26.6, 28.1, 28.4, 31.5, 32.7, 118.7, 120.1, 124.7, 128.1, 128.8, 130.9, 131.2, 131.5, 134.5, 137.9, 140.6, 141.7; MS (EI) m/z (%): 339 (100.0) [M-N_2^+], 341 (98.0), 310 (39.5), 285 (23.1), 260 (20.9), 230 (37.7), 217 (51.5), 204 (75.7); HRMS (EI) Calcd. for $C_{19}H_{18}NBr$ (M-N_2^+) requires 339.0623, found: 339.0626.

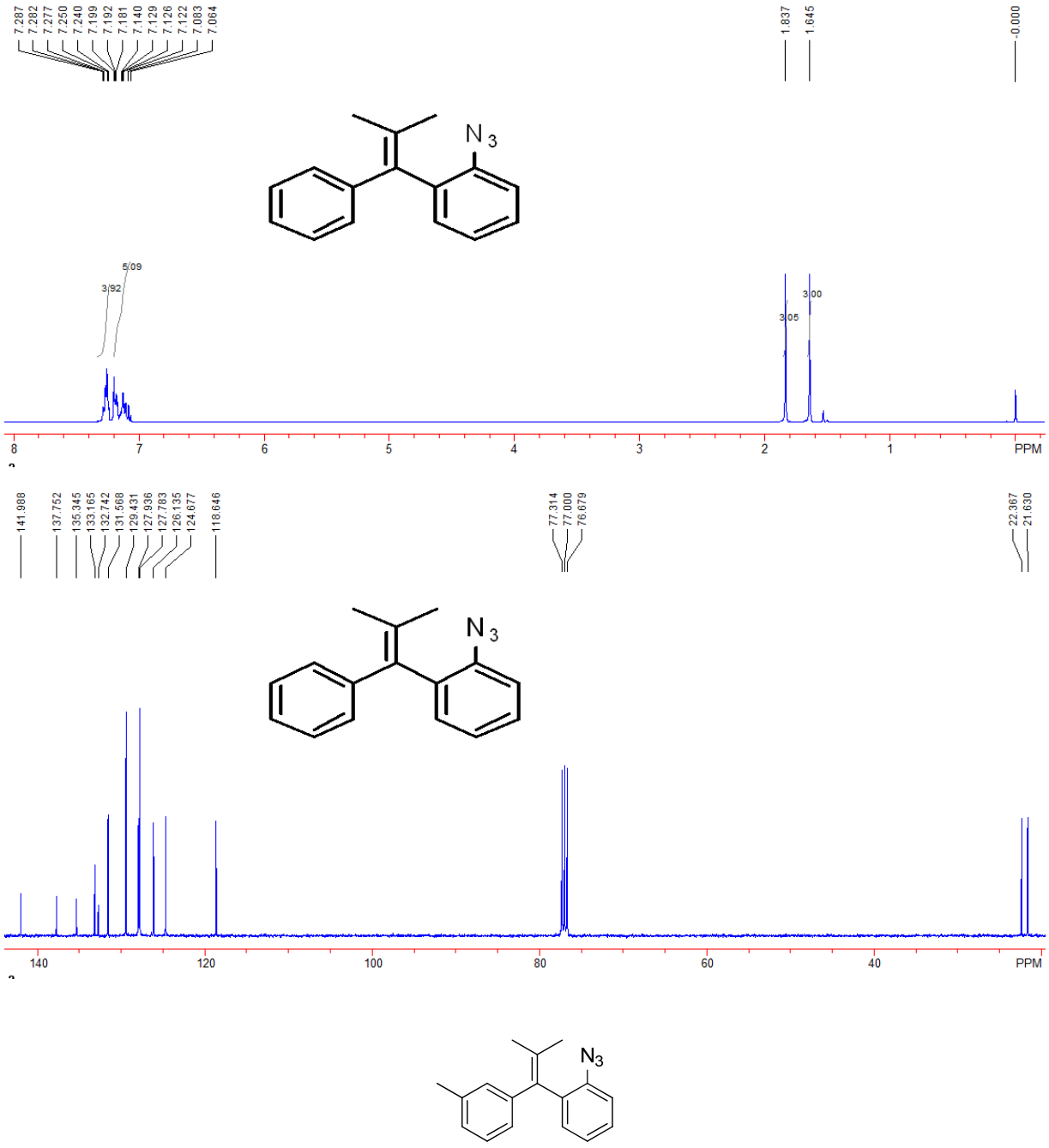


Compound 3k: 165 mg, 51%, A yellow solid, m.p. 77-79 ^{o}C; IR (CH_2Cl_2): ν 2927, 2853, 2124, 2094, 1479, 1297, 807 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 1.50-1.65 (m, 6H), 2.01 (t, *J* = 5.6 Hz, 2H), 2.25 (t, *J* = 5.6 Hz, 2H), 7.03 (d, *J* = 8.4 Hz, 1H), 7.12 (d, *J* = 2.4 Hz, 1H), 7.16-7.22 (m, 4H), 7.26-7.30 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 26.6, 28.0, 28.3, 31.5, 32.7, 119.9, 126.4, 127.8, 127.9, 128.7, 129.4, 129.8, 131.3, 136.6, 136.7, 141.0, 141.9; MS (EI) m/z (%): 295 (100.0) [M-N_2^+], 294 (46.3), 266 (49.0), 254 (18.6), 240 (31.4), 230 (22.1), 205 (27.1), 190 (15.7); HRMS (EI) Calcd. for $C_{19}H_{18}NCl$ (M-N_2^+) requires 295.1128, found: 295.1125.

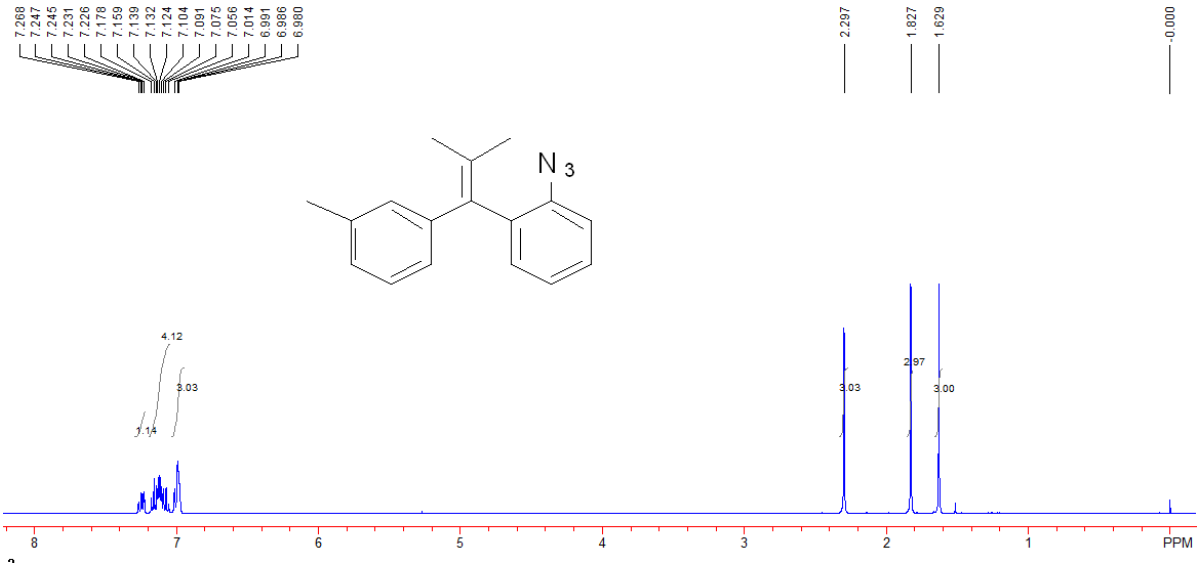


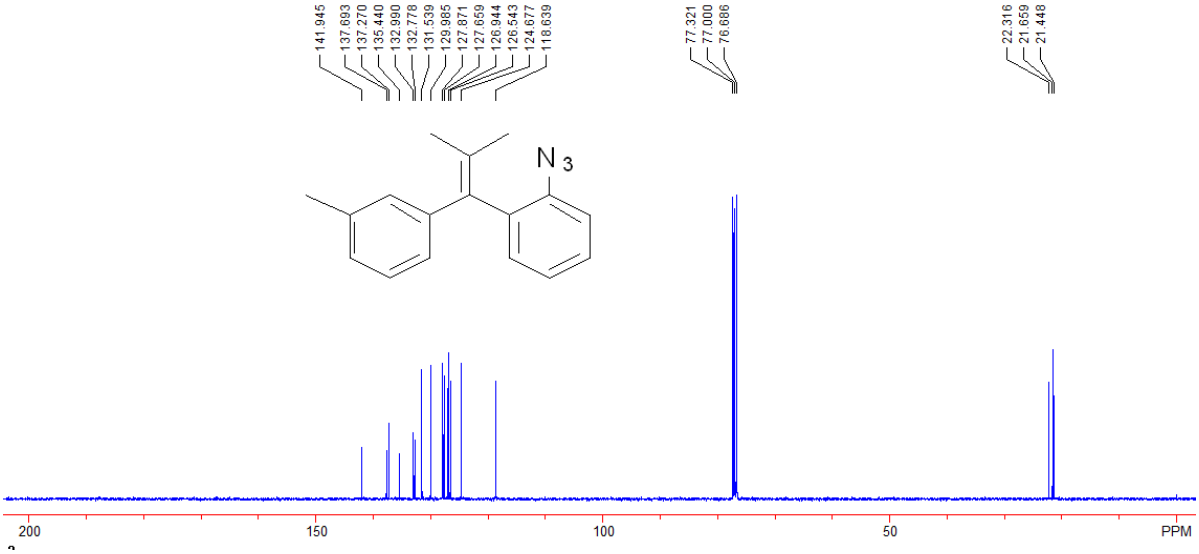


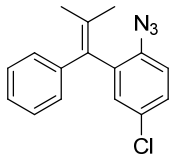
Compound 3l: 167 mg, 67%, A yellow solid, m.p. 45-47 ^{o}C; IR (CH_2Cl_2): ν 3018, 2910, 2121, 2086, 1487, 1288, 751 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 1.65 (s, 3H), 1.84 (s, 3H), 7.06-7.20 (m, 5H), 7.24-7.29 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 21.6, 22.4, 118.6, 124.7, 126.1, 127.8, 127.9, 129.4, 131.6, 132.7, 133.2, 135.3, 137.8, 142.0; MS (EI) m/z (%): 221 (100.0) [M-N_2^+], 220 (77.0), 206 (57.2), 204 (28.7), 178 (23.9), 165 (42.3), 152 (9.0), 115 (7.8); HRMS (EI) Calcd. for $C_{16}H_{15}N$ (M-N_2^+) requires 221.1204, found: 221.1205.



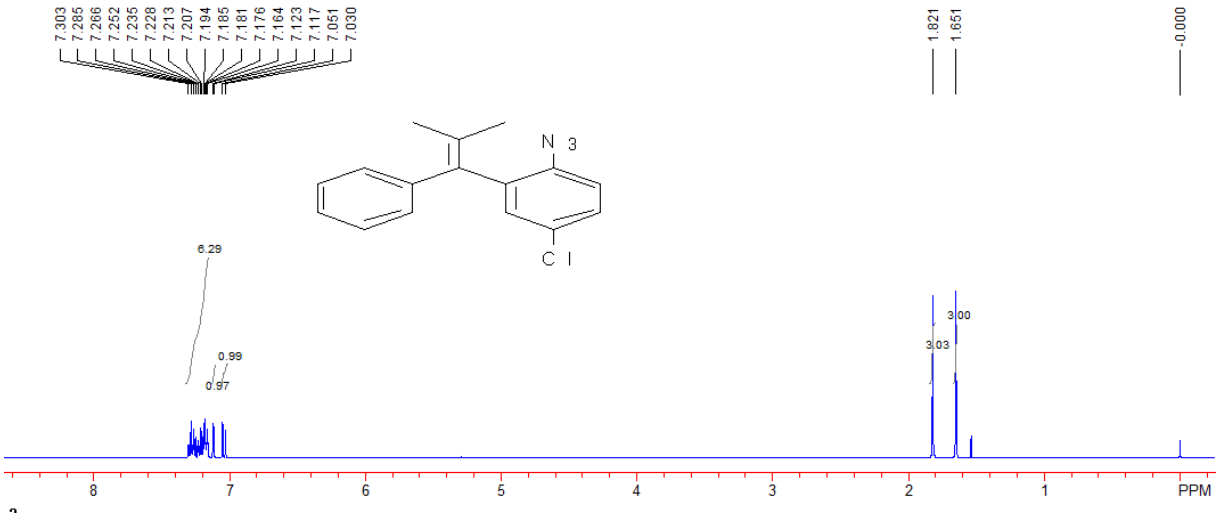
Compound 3m: 200 mg, 76%, A yellow liquid; IR (CH_2Cl_2): ν 3020, 2910, 2119, 2082, 1572, 1483, 1282, 750 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$, TMS): δ 1.63 (s, 3H), 1.83 (s, 3H), 2.30 (s, 3H), 6.98-7.01 (m, 3H), 7.06-7.18 (m, 4H), 7.23-7.27 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 21.4, 21.7, 22.3, 118.6, 124.7, 126.5, 126.9, 127.7, 127.9, 130.0, 131.5, 132.8, 133.0, 135.4, 137.3, 137.7, 141.9; MS (EI) m/z (%): 235 (100.0) [M-N_2^+], 234 (74.0), 220 (55.5), 218 (17.4), 2.4 (30.0), 179 (31.5), 165 (8.4), 152 (8.3); HRMS (EI) Calcd. for $C_{17}H_{17}N$ (M-N_2^+) requires 235.1361, found: 235.1366.







Compound 3n: 224 mg, 79%, A yellow solid, m.p. 63-65 ^{o}C; IR (CH_2Cl_2): ν 3020, 2910, 2118, 2082, 1573, 1483, 1283, 750 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 1.65 (s, 3H), 1.82 (s, 3H), 7.04 (d, *J* = 8.4 Hz, 1H), 7.12 (d, *J* = 2.4 Hz, 1H), 7.16-7.30 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 21.6, 22.4, 119.9, 126.4, 127.9, 129.4, 129.8, 131.3, 131.7, 134.2, 136.5, 136.8, 141.3; MS (EI) m/z (%): 255 (100.0) [M-N_2^+], 254 (71.3), 218 (15.7), 204 (46.3), 178 (50.1), 152 (10.9), 115 (10.3), 102 (13.4); HRMS (EI) Calcd. for $C_{16}H_{14}NCl$ (M-N_2^+) requires 255.0815, found: 255.0817.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7.030
1.821
1.651
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C l
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0.97
3.03
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7
6
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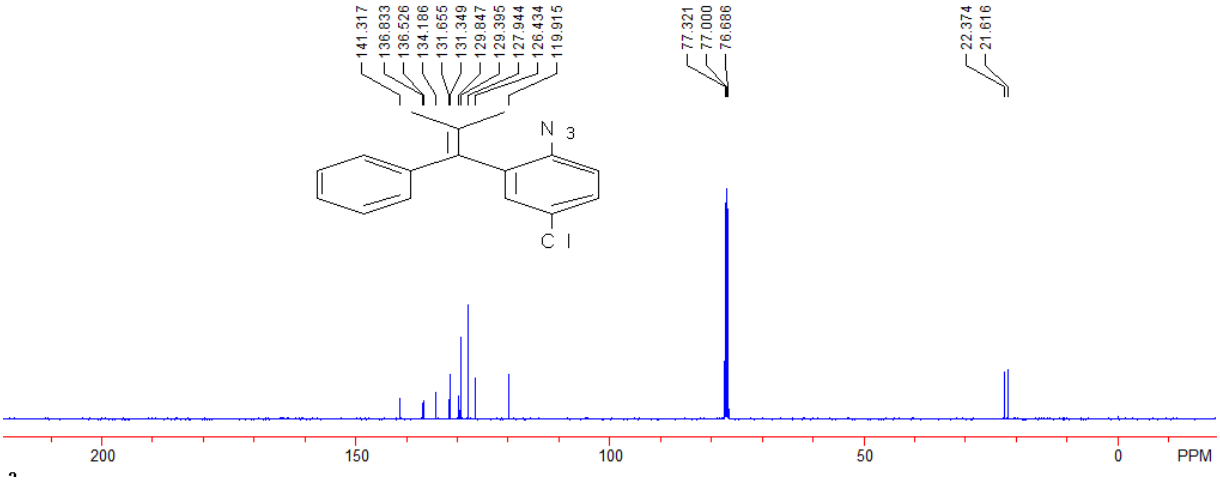
PPM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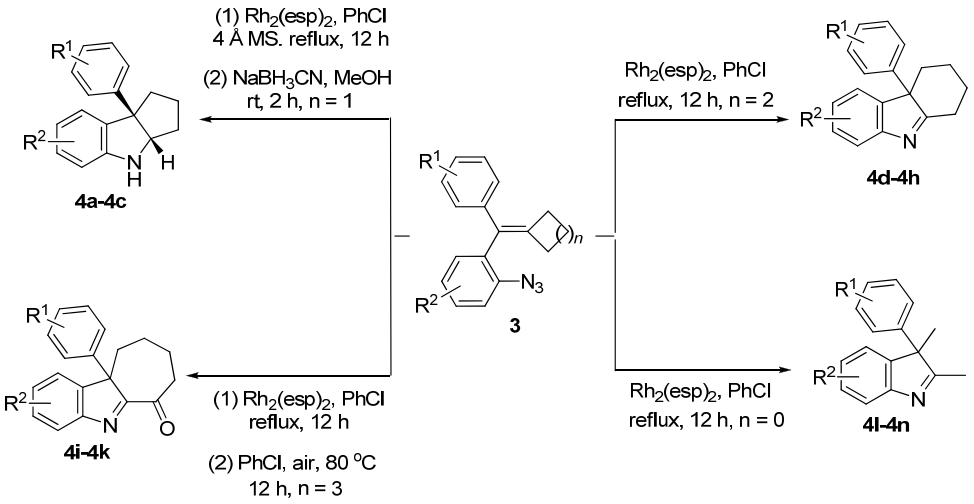
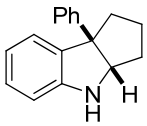
General procedure for the synthesis of compounds 4

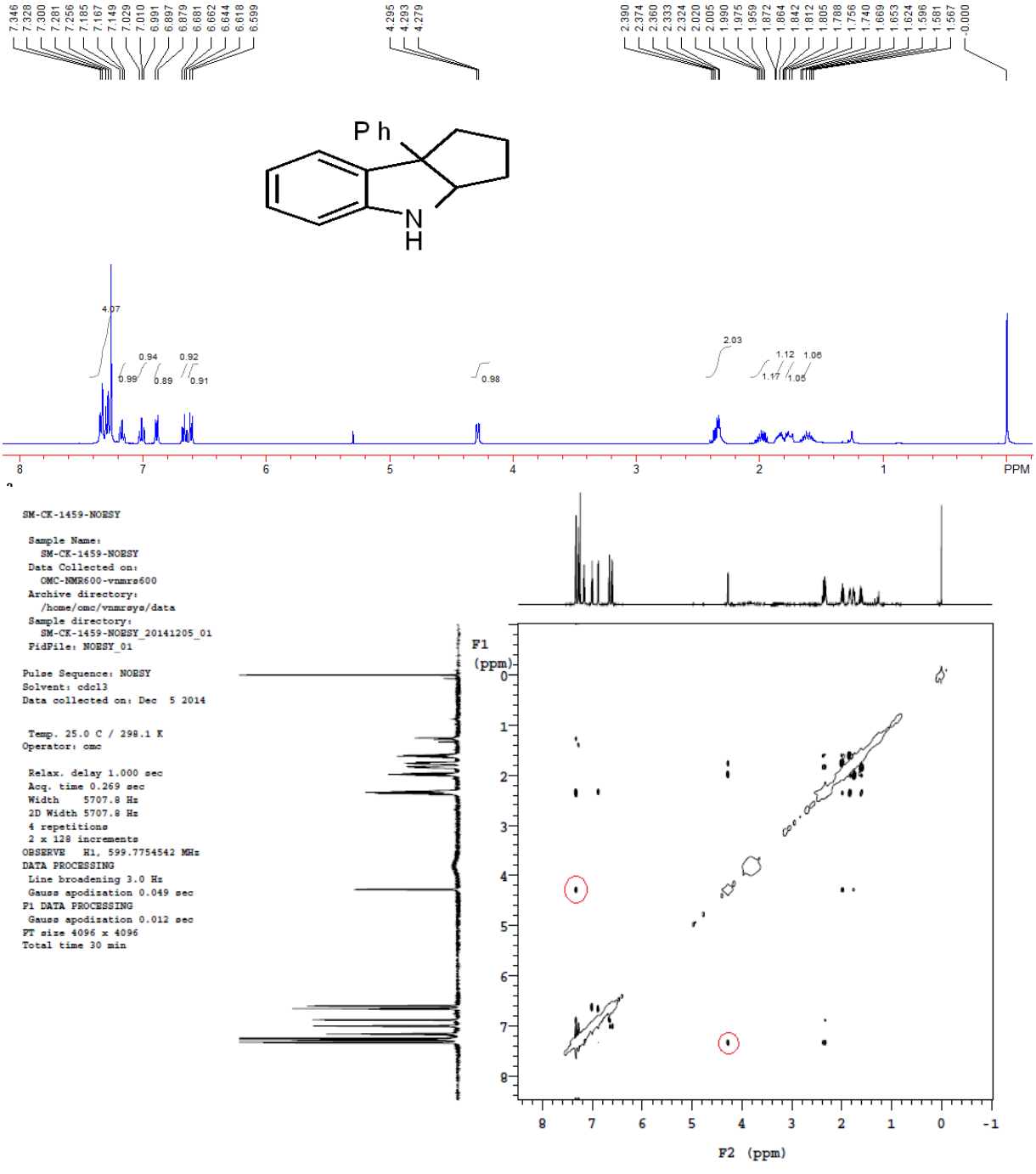


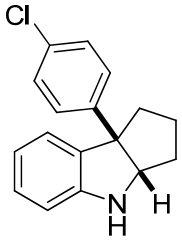
A solution of compound **3** (0.1 mmol) and $Rh_2(esp)_2$ (3.8 mg, 0.005 mmol) in dry chlorobenzene (0.5 mL) was stirred at 130 ^oC for 12 h. Afterwards, when n = 1, $NaBH_3CN$ (31 mg, 0.5 mmol) in MeOH (1 mL) was added and the mixture was stirred at room temperature for another 2 h. When n = 3, the mixture was stirred in air 80 ^oC for another 12 h. Then the solvent was removed under reduced pressure and the residue was purified by silica gel flash chromatography (eluent: petroleum ether / ethyl acetate = 10 / 1) to afford the product in moderate to high yield.

Spectroscopic data for all products 4

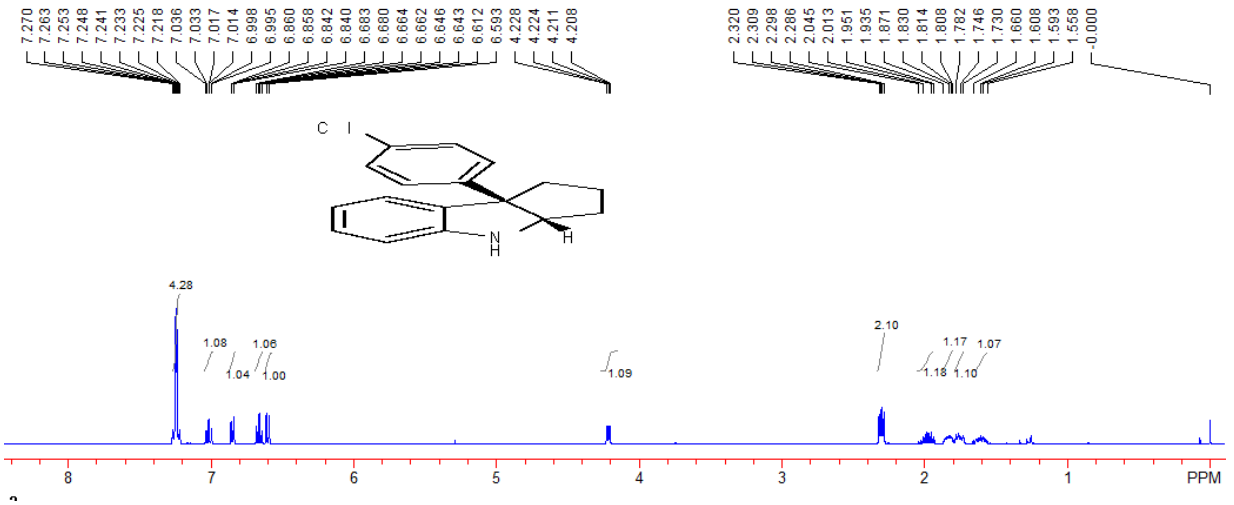


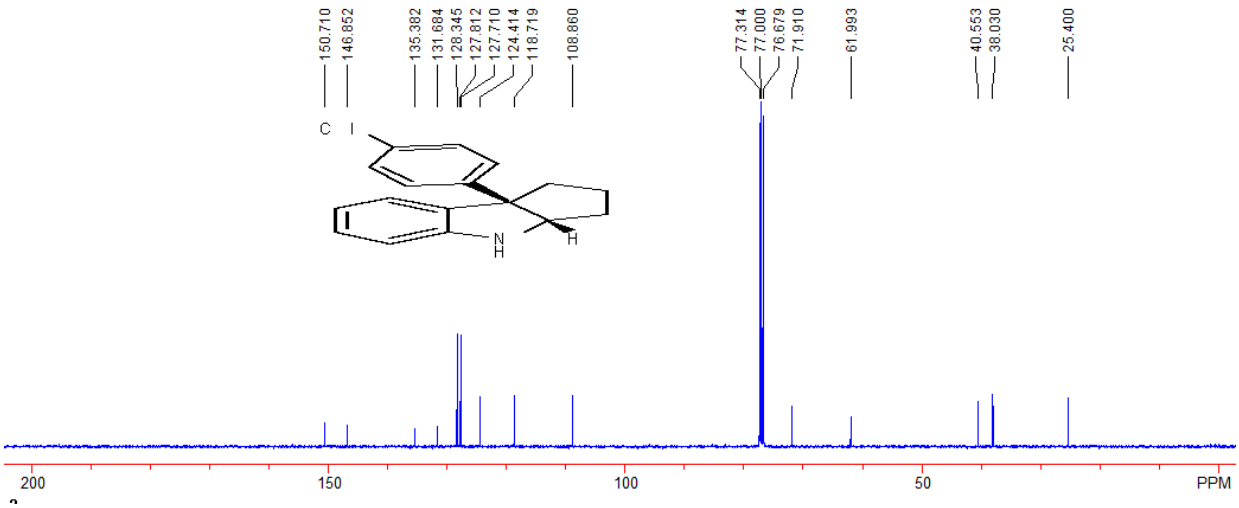
Compound 4a: 14 mg, 60%, A known compound;[4] ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 1.57-1.76 (m, 1H), 1.79-1.81 (m, 1H), 1.84-1.87 (m, 1H), 1.96-2.02 (m, 1H), 2.32-2.39 (m, 2H), 4.28-4.30 (m, 1H), 6.61 (d, J = 7.6 Hz, 1H), 6.66 (dd, J_1 = J_2 = 7.2 Hz, 1H), 6.89 (d, J = 7.2 Hz, 1H), 7.01 (dd, J_1 = J_2 = 7.6 Hz, 1H), 7.17 (dd, J_1 = J_2 = 7.2 Hz, 1H), 7.26-7.35 (m, 4H).

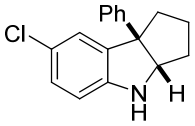




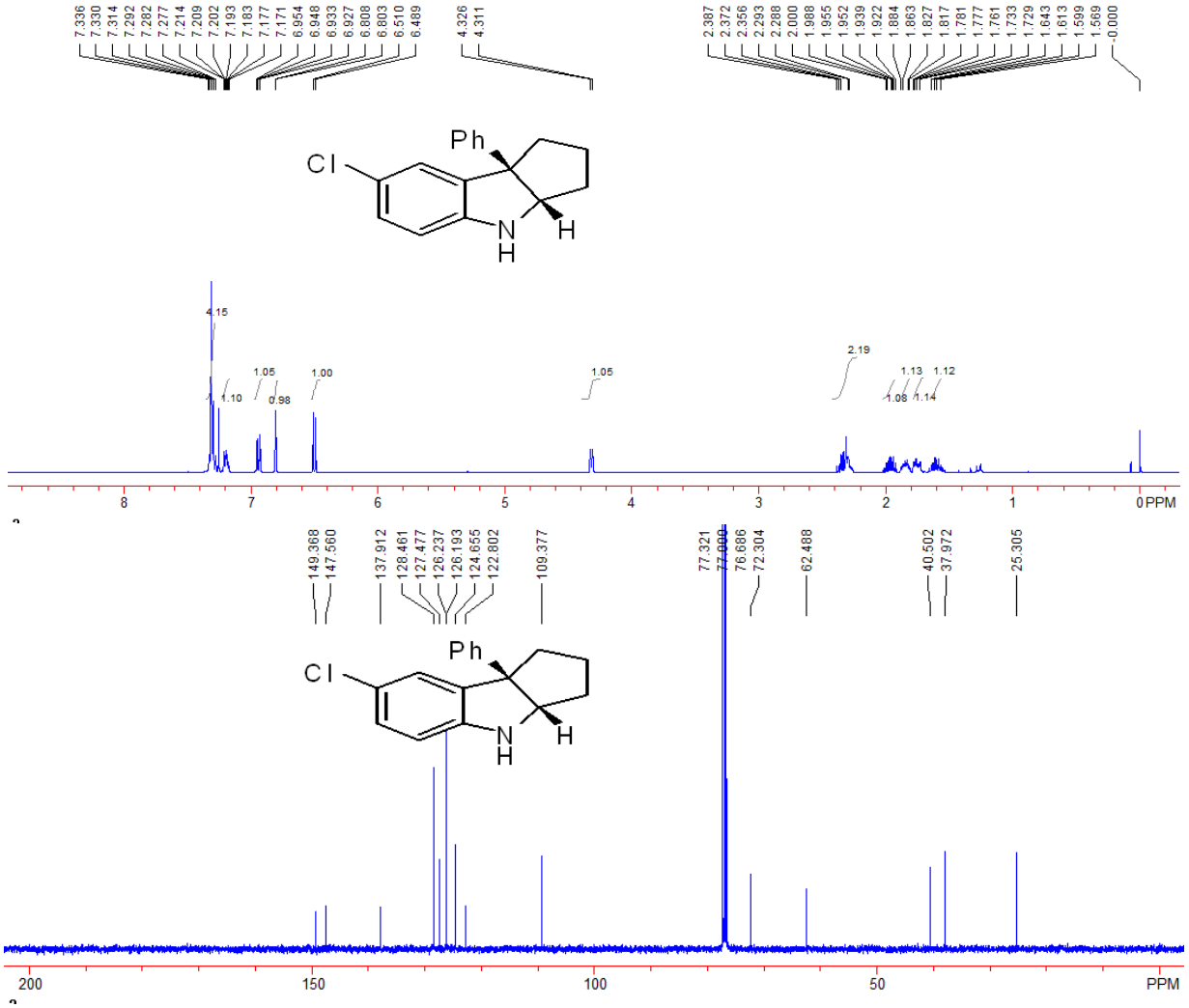
Compound 4b: 16 mg, 59%, A red liquid; IR (CH_2Cl_2): ν 3398, 2950, 2865, 1603, 1483, 1258, 1092, 741 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$, TMS): δ 1.56-1.66 (m, 1H), 1.73-1.78 (m, 1H), 1.81-1.87 (m, 1H), 1.94-2.05 (m, 1H), 2.29-2.32 (m, 2H), 4.21-4.23 (m, 1H), 6.60 (d, J = 7.6 Hz, 1H), 6.66 (ddd, J_1 = J_2 = 7.6 Hz, J_3 = 1.2 Hz, 1H), 6.85 (dd, J_1 = 7.2 Hz, J_2 = 0.8 Hz, 1H), 7.01 (ddd, J_1 = J_2 = 7.6 Hz, J_3 = 1.2 Hz, 1H), 7.22-7.27 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 25.4, 38.0, 40.6, 62.0, 71.9, 108.9, 118.7, 124.4, 127.7, 127.8, 128.3, 131.7, 135.4, 146.9, 150.7; MS (ESI) *m/z*: 270.1 ($M+H^+$, 100); HRMS (ESI) Calcd. for $C_{17}H_{17}ClN^+$ requires 270.1044, found: 270.1054.

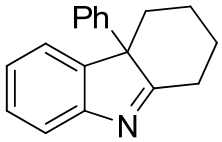




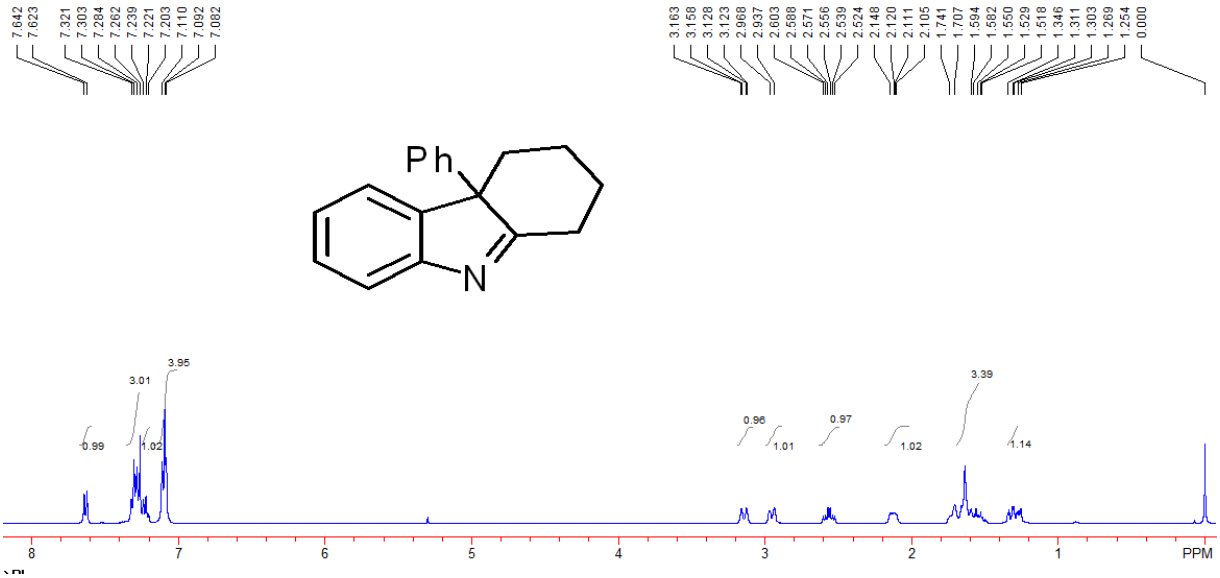


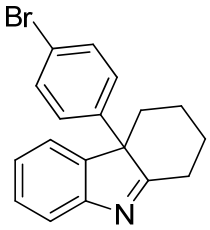
Compound 4c: 16 mg, 60%, A red liquid; IR (CH_2Cl_2): ν 3408, 2951, 2867, 1600, 1480, 1427, 1260, 700 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$, TMS): δ 1.57-1.64 (m, 1H), 1.73-1.78 (m, 1H), 1.82-1.88 (m, 1H), 1.92-2.00 (m, 1H), 2.29-2.39 (m, 2H), 4.32 (d, J = 6.0 Hz, 1H), 6.50 (d, J = 8.4 Hz, 1H), 6.80 (d, J = 2.0 Hz, 1H), 6.94 (dd, J_1 = 8.4 Hz, J_2 = 2.4 Hz, 1H), 7.17-7.21 (m, 1H), 7.28-7.34 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 25.3, 38.0, 40.5, 62.5, 72.3, 109.4, 122.8, 124.7, 126.19; 126.24, 127.5, 128.5, 137.9, 147.6, 149.4; MS (ESI) *m/z*: 270.1 ($M+H^+$, 100); HRMS (ESI) Calcd. for $C_{17}H_{17}ClN^+$ requires 270.1044, found: 270.1052.



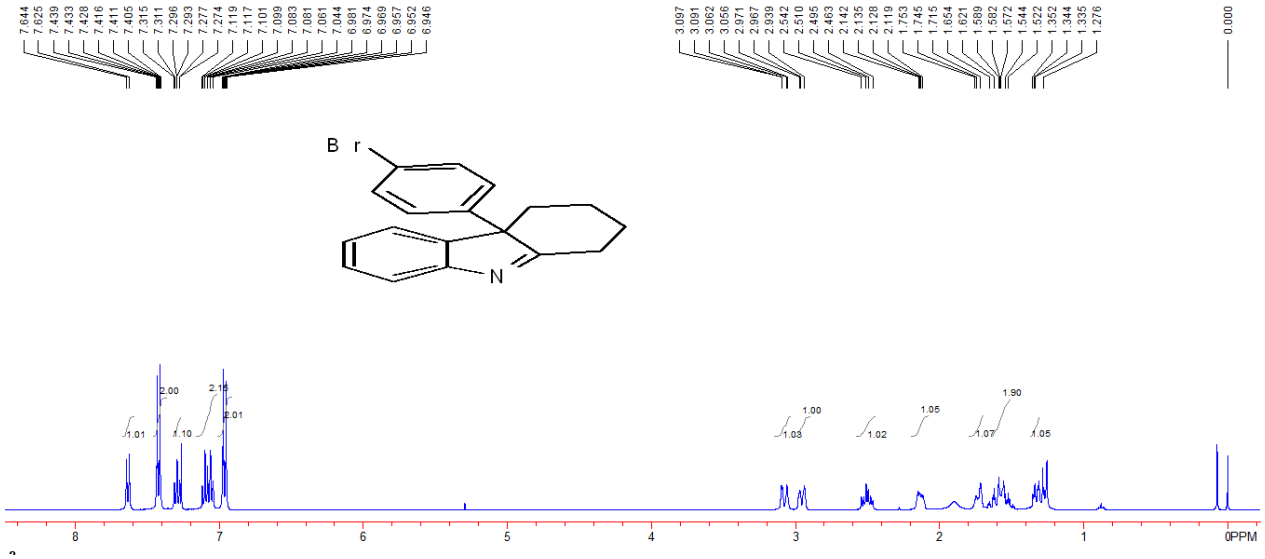


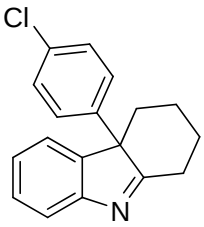
Compound 4d: 18 mg, 73%, A known compound;[4] ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 1.25-1.35 (m, 1H), 1.52-1.74 (m, 3H), 2.11-2.15 (m, 1H), 2.52-2.60 (m, 1H), 2.94-2.97 (m, 1H), 3.14 (dd, J_1 = 14.0 Hz, , J_2 = 2.0 Hz, 1H), 7.08-7.11 (m, 4H), 7.20-7.24 (m, 1H), 7.26-7.32 (m, 3H), 7.63 (d, J = 7.6 Hz, 1H).



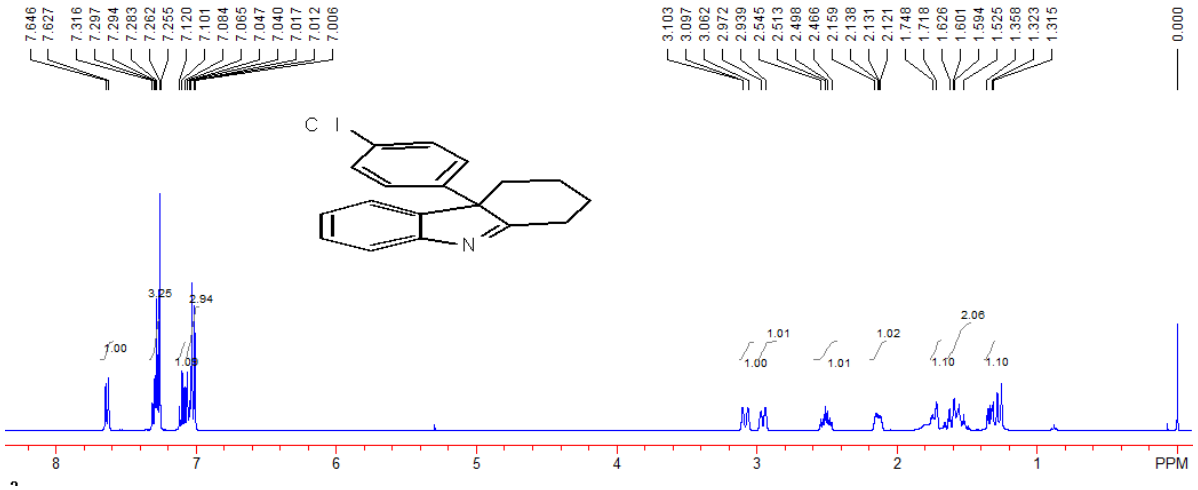


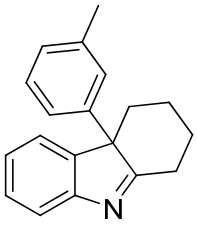
Compound 4e: 20 mg, 62%, A known compound;[4] ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 1.28-1.35 (m, 1H), 1.52-1.65 (m, 2H), 1.72-1.75 (m, 1H), 2.12-2.14 (m, 1H), 2.46-2.54 (m, 1H), 2.94-2.97 (m, 1H), 3.08 (dd, J_1 = 14.0 Hz, , J_2 = 2.4 Hz, 1H), 6.95-6.98 (m, 2H), 7.04-7.12 (m, 2H), 7.27-7.32 (m, 1H), 7.41-7.44 (m, 2H), 7.63 (d, J = 7.6 Hz, 1H).



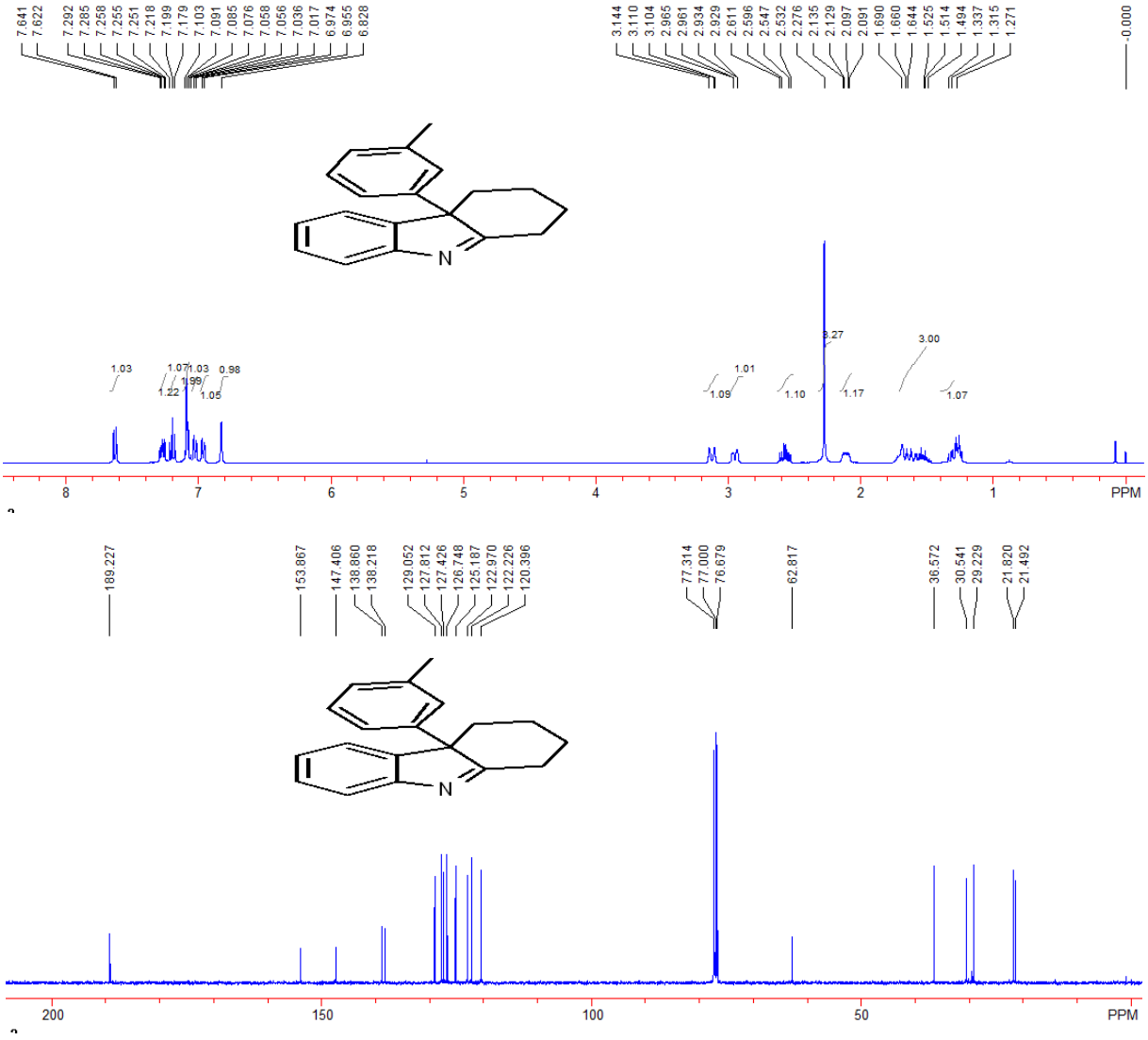


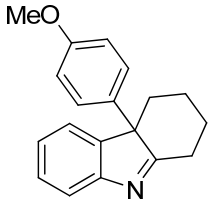
Compound 4f: 19 mg, 68%, A known compound;[4] ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 1.32-1.36 (m, 1H), 1.53-1.63 (m, 2H), 1.72-1.75 (m, 1H), 2.12-2.16 (m, 1H), 2.47-2.55 (m, 1H), 2.94-2.97 (m, 1H), 3.06-3.10 (m, 1H), 7.01-7.05 (m, 3H), 7.07-7.12 (m, 1H), 7.26-7.32 (m, 3H), 7.64 (d, *J* = 7.6 Hz, 1H).



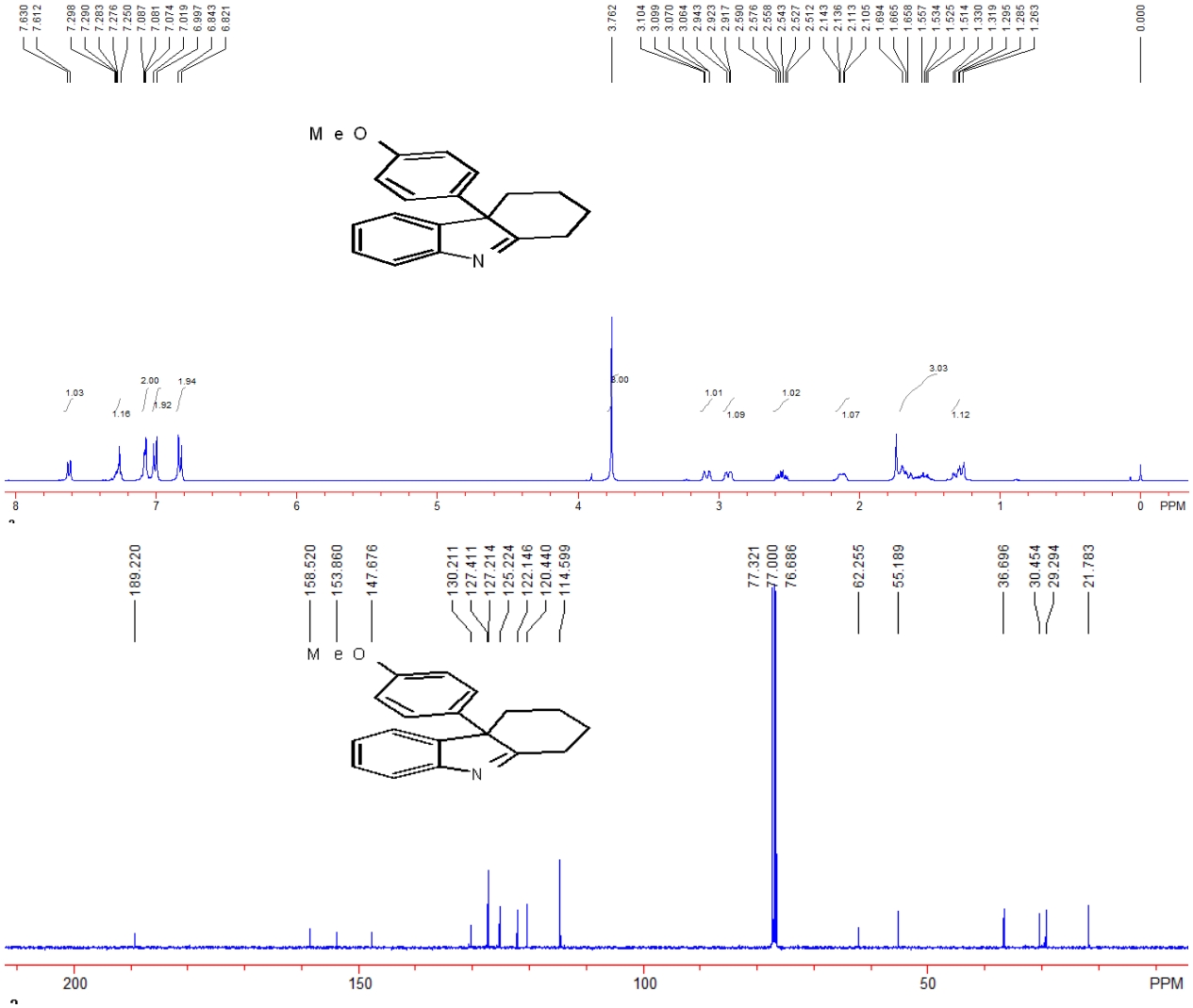


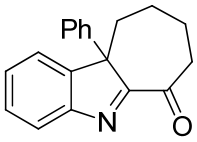
Compound 4g: 21 mg, 80%, A yellow solid, m.p. 78-80 ^{o}C; IR (CH_2Cl_2): ν 3041 2934, 2858, 1581, 1450, 768, 701 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 1.27-1.34 (m, 1H), 1.49-1.69 (m, 3H), 2.09-2.14 (m, 1H), 2.28 (s, 3H), 2.53-2.61 (m, 1H), 2.93-2.97 (m, 1H), 3.10-3.14 (m, 1H), 6.83 (s, 1H), 6.96 (d, *J* = 7.6 Hz, 1H), 7.03 (d, *J* = 7.6 Hz, 1H), 7.06-7.10 (m, 2H), 7.20 (dd, J_1 = J_2= 8.0 Hz, 1H), 7.25-7.29 (m, 1H), 7.63 (d, *J* = 7.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 21.5, 21.8, 29.2, 30.5, 36.6, 62.8, 120.4, 122.2, 123.0, 125.2; 126.7, 127.4, 127.8, 129.1, 138.2, 138.9, 147.4, 153.9, 189.2; MS (ESI) *m/z*: 262.2 (M+H^{+}, 100); HRMS (ESI) Calcd. for $C_{19}H_{20}N^{+}$ requires 262.1590, found: 262.1600.



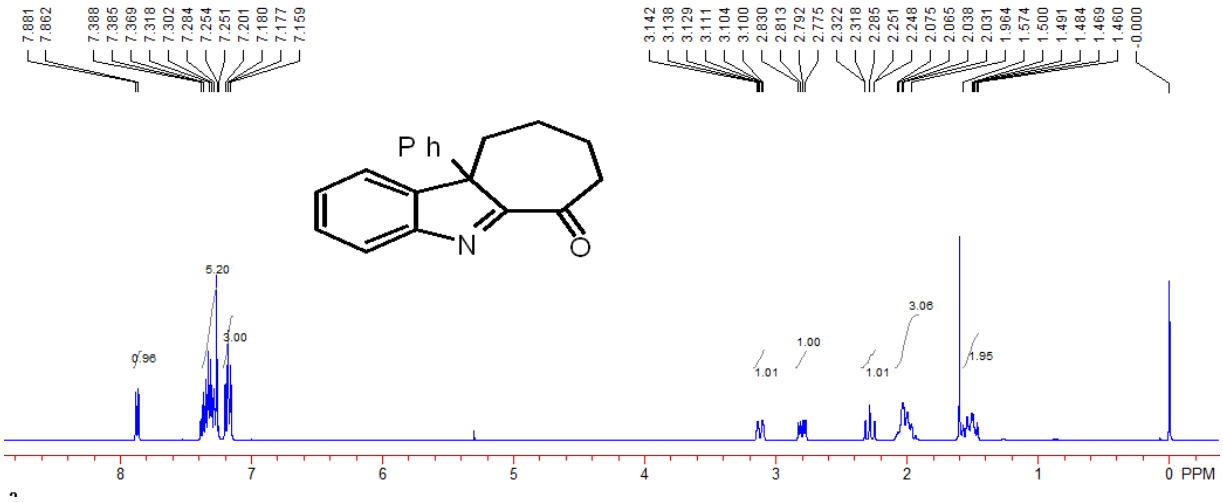


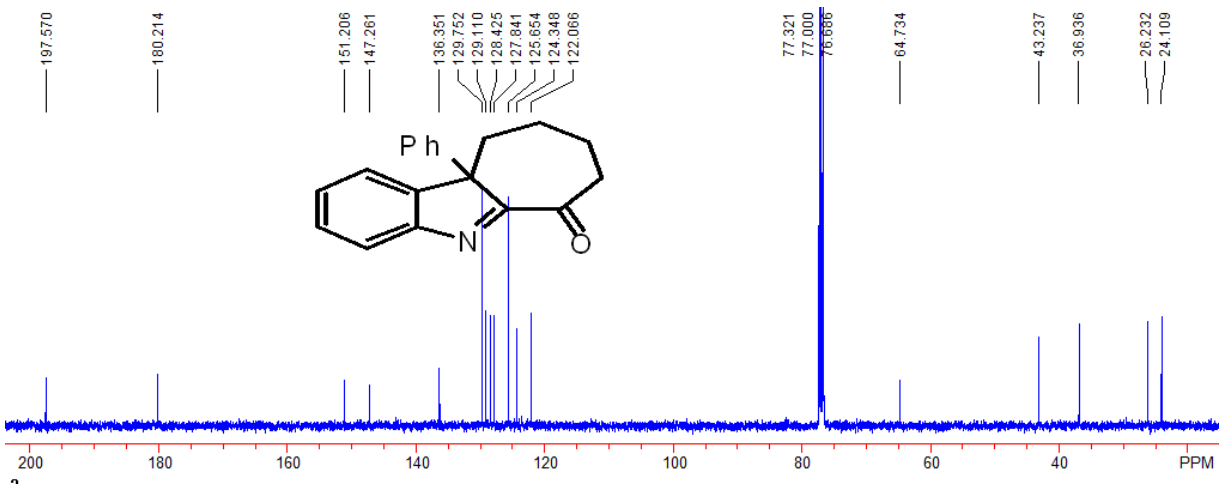
Compound 4h: 20 mg, 72%, A yellow solid, m.p. 128-130 ^{o}C; IR (CH_2Cl_2): ν 3057 2936, 2859, 1581, 1510, 1454, 1034, 820 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 1.26-1.33 (m, 1H), 1.51-1.69 (m, 3H), 2.11-2.14 (m, 1H), 2.51-2.59 (m, 1H), 2.92-2.94 (m, 1H), 3.06-3.10 (m, 1H), 3.76 (s, 3H), 6.83 (d, *J* = 8.8 Hz, 2H), 7.01 (d, *J* = 8.8 Hz, 2H), 7.07-7.09 (m, 2H), 7.25-7.30 (m, 1H), 7.62 (d, *J* = 7.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 21.8, 29.3, 30.5, 36.7, 55.2, 62.3, 114.6, 120.4, 122.1, 125.2; 127.2, 127.4, 130.2, 147.7, 153.9, 158.5, 189.2; MS (ESI) *m/z*: 278.2 ($M+H^+$, 100); HRMS (ESI) Calcd. for $C_{19}H_{20}NO^+$ requires 278.1545, found: 278.1560.

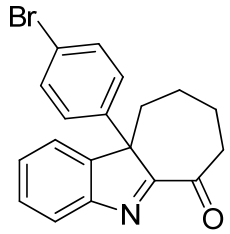




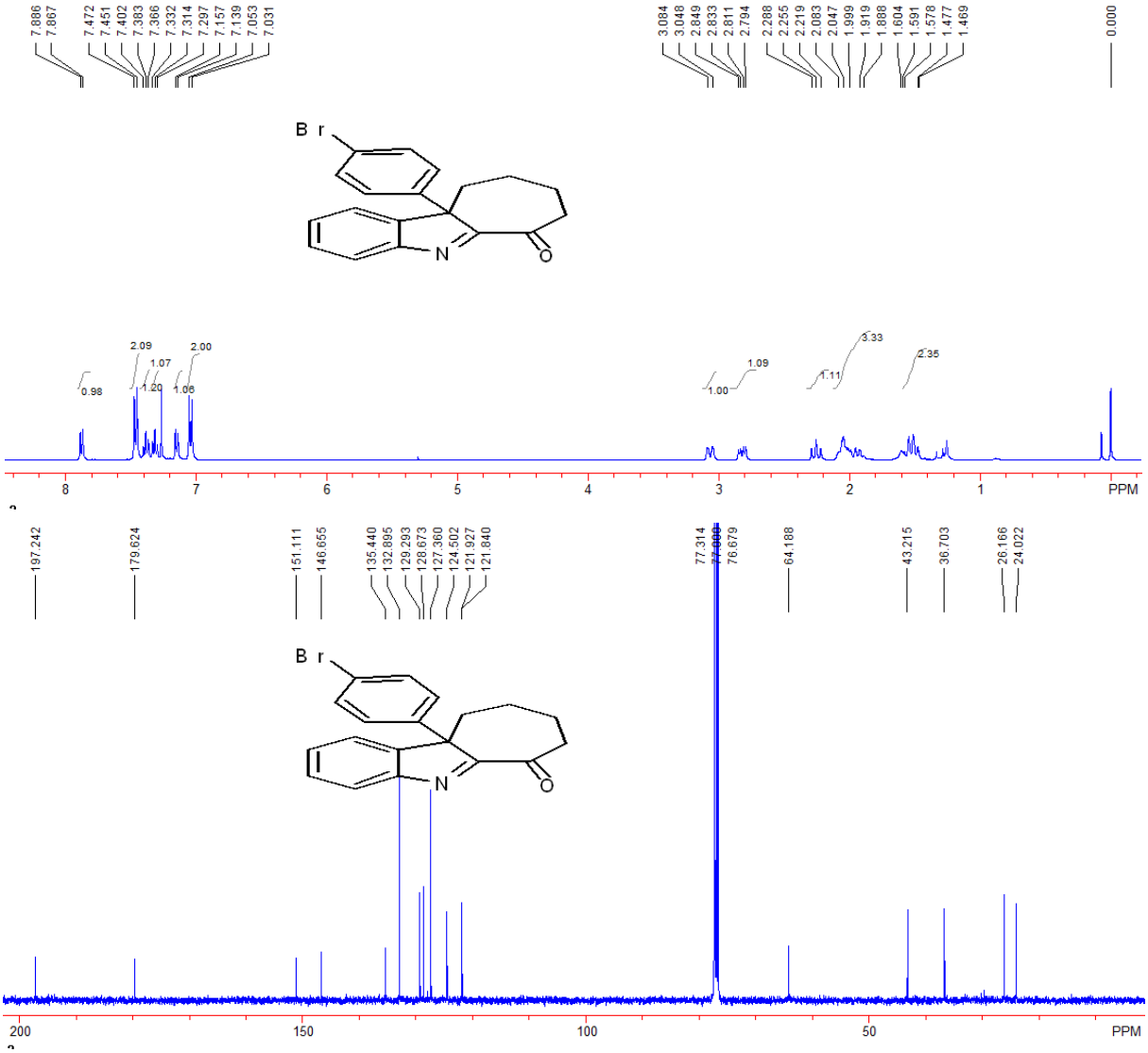
Compound 4i: 21 mg, 75%, A yellow solid, m.p. 170-172 ^{o}C; IR (CH_2Cl_2): ν 3060, 2931, 1692, 1526, 1451, 771 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 1.46-1.57 (m, 2H), 1.96-2.08 (m, 3H), 2.25-2.32 (m, 1H), 2.80 (dd, J_1 = 15.2 Hz, J_2 = 6.8 Hz, 1H), 3.10-3.14 (m, 1H), 7.16-7.20 (m, 3H), 7.25-7.39 (m, 5H), 7.87 (d, J = 7.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 24.1, 26.2, 36.9, 43.2, 64.7, 122.1, 124.3, 125.7, 127.8, 128.4, 129.1, 129.8, 136.4, 147.3, 151.2, 180.2, 197.6; MS (ESI) *m/z*: 276.1 (M+H^{+}, 100); HRMS (ESI) Calcd. for $C_{19}H_{18}NO^{+}$ requires: 276.1383, found: 276.1386.

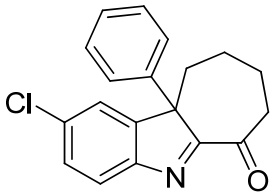




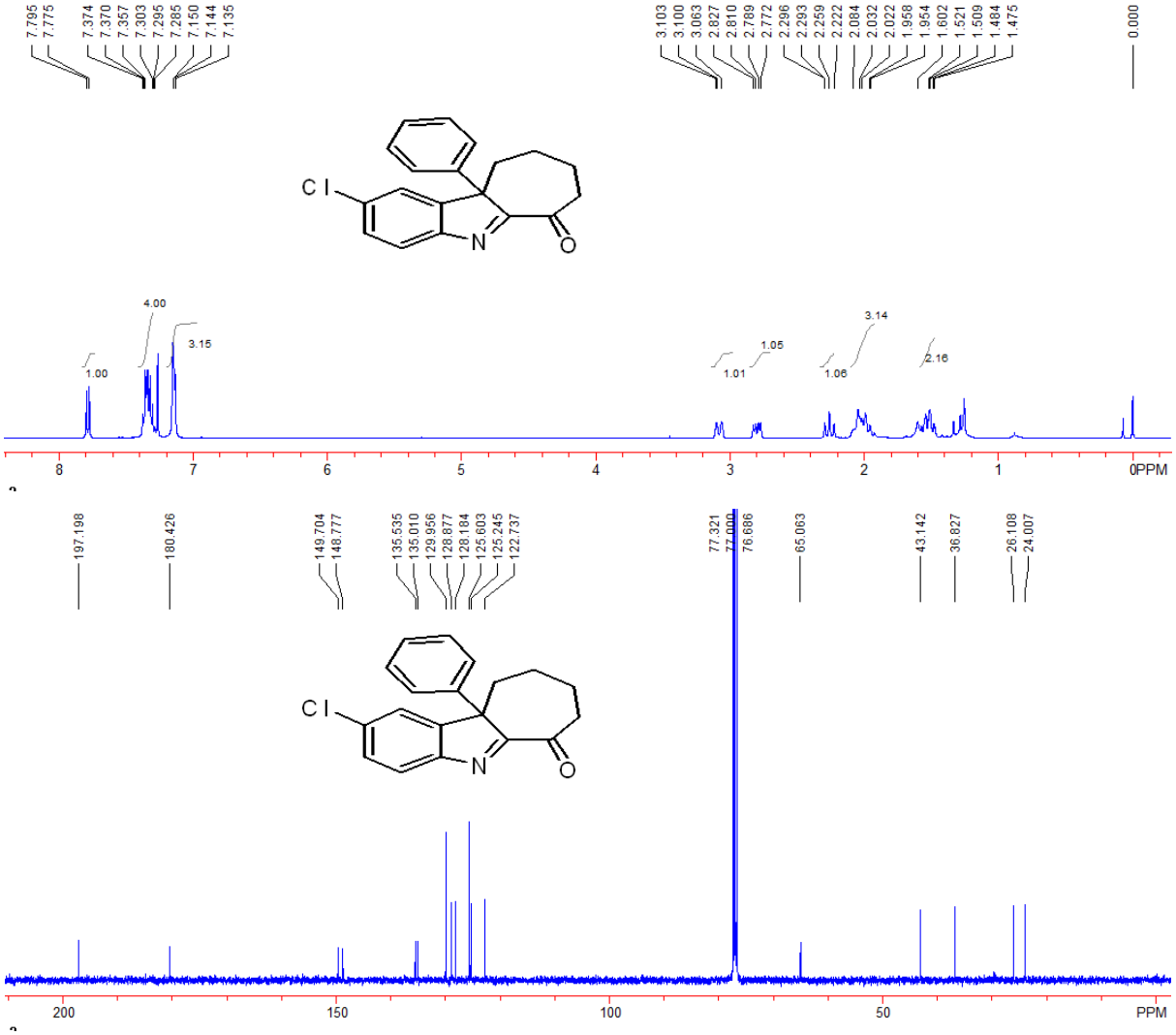


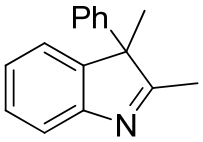
Compound 4j: 20 mg, 62%, A yellow solid, m.p. 196-198 ^{o}C; IR (CH_2Cl_2): ν 2930, 2855, 1692, 1275, 1084, 1009, 750 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 1.47-1.60 (m, 2H), 1.89-2.08 (m, 3H), 2.22-2.29 (m, 1H), 2.82 (dd, J_1 = 15.6 Hz, J_2 = 6.8 Hz, 1H), 3.07 (d, J = 14.4 Hz, 1H), 7.04 (d, J = 8.8 Hz, 2H), 7.15 (d, J = 7.2 Hz, 1H), 7.31 (dd, J_1 = J_2= 6.8 Hz, 1H), 7.38 (dd, J_1 = J_2= 6.8 Hz, 1H), 7.46 (d, J = 8.4 Hz, 2H), 7.88 (d, J = 7.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 24.0, 26.2, 36.7, 43.2, 64.2, 121.8, 121.9, 124.5, 127.4, 128.7, 129.3, 132.9, 135.4, 146.7, 151.1, 179.6, 197.2; MS (ESI) *m/z*: 354.1 (M+H^{+}, 100); HRMS (ESI) Calcd. for $C_{19}H_{17}BrNO^{+}$ requires: 354.0488, found: 354.0500.



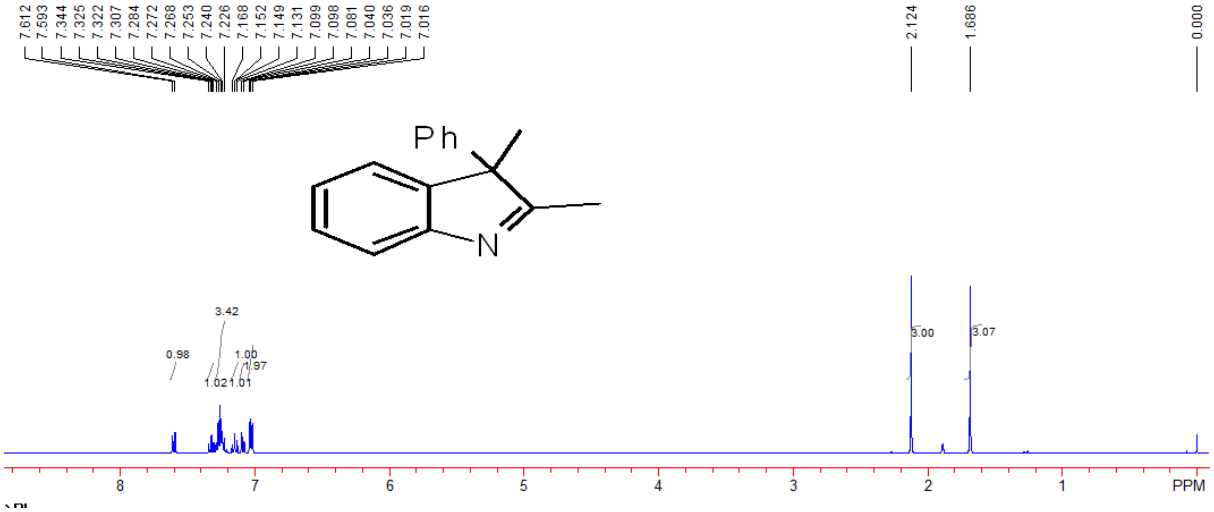


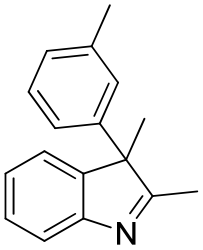
Compound 4k: 19 mg, 62%, A yellow solid, m.p. 180-182 ^{o}C; IR (CH_2Cl_2): ν 3057, 2930, 2855, 1691, 1065, 825, 734, 700 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 1.48-1.60 (m, 2H), 1.95-2.08 (m, 3H), 2.22-2.30 (m, 1H), 2.80 (dd, J_1 = 15.2 Hz, J_2 = 6.8 Hz, 1H), 3.06-3.10 (m, 1H), 7.14-7.15 (m, 3H), 7.29-7.37 (m, 4H), 7.79 (d, J = 8.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 24.0, 26.1, 36.8, 43.1, 65.1, 122.7, 125.2, 125.6, 128.2, 128.9, 130.0, 135.0, 135.5, 148.8, 149.7, 180.4, 197.2; MS (ESI) *m/z*: 310.1 ($M+H^+$, 100); HRMS (ESI) Calcd. for $C_{19}H_{17}ClNO^+$ requires: 310.0993, found: 310.1003.



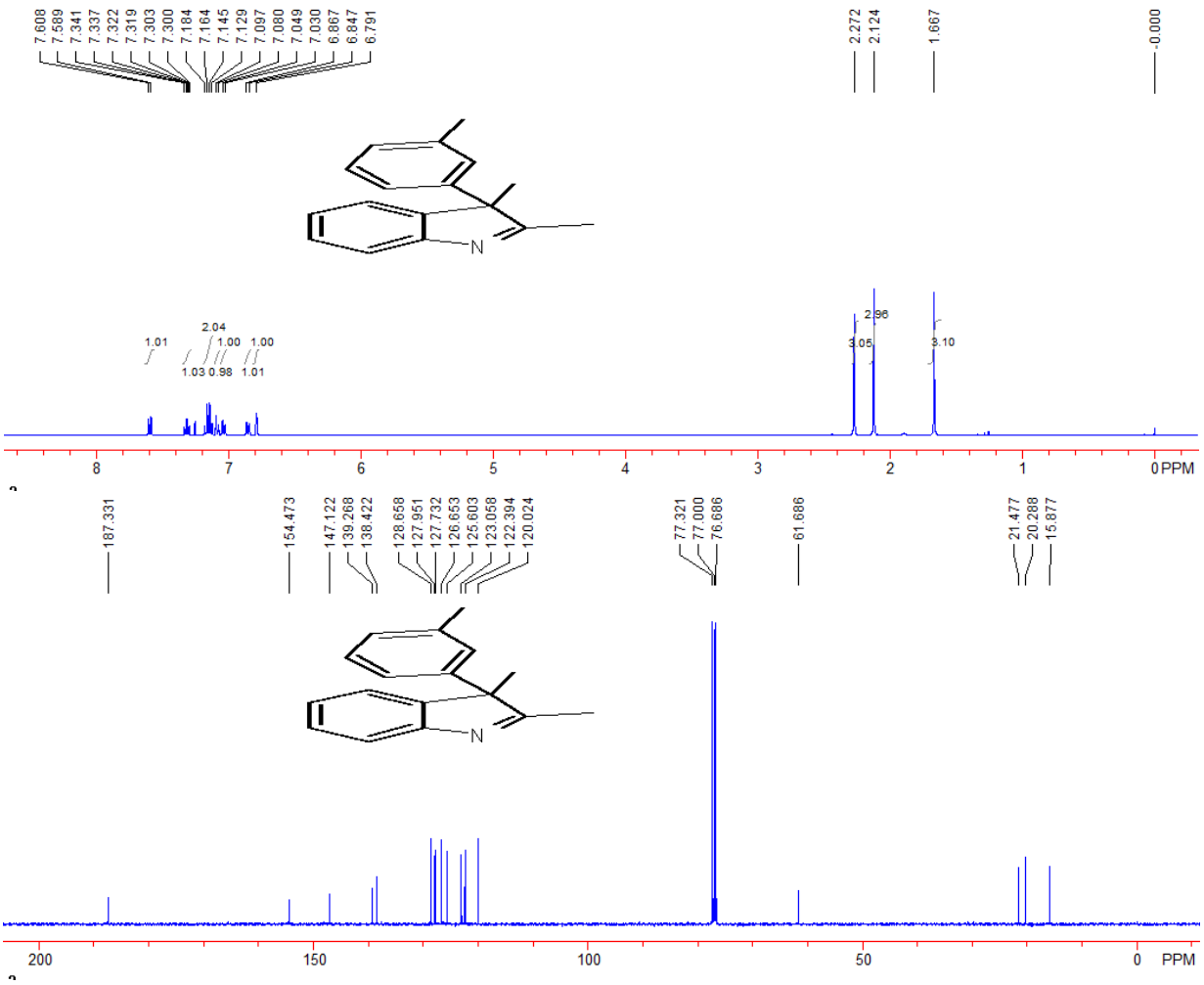


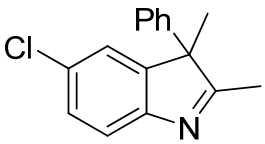
Compound 4l: 20 mg, 88%, A known compound;[4] ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 1.69 (s, 3H), 2.12 (s, 3H), 7.03 (dd, J_1 = 8.0 Hz, J_2 = 1.2 Hz, 1H), 7.08-7.10 (m, 1H), 7.13-7.17 (m, 1H), 7.23-7.28 (m, 3H), 7.31-7.34 (m, 1H), 7.60 (d, J = 7.6 Hz, 1H).



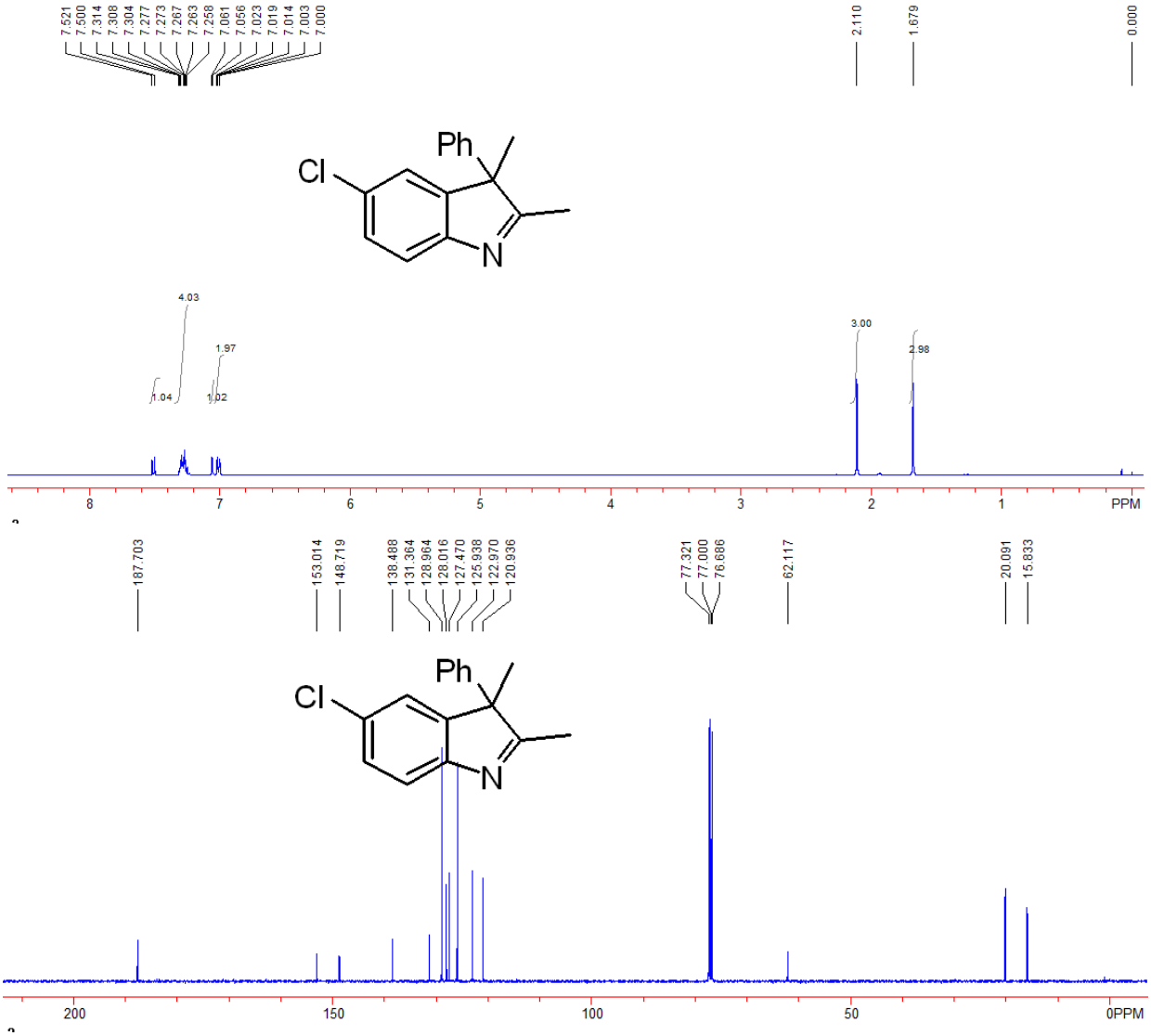


Compound 4m: 19 mg, 81%, A yellow liquid; IR (CH_2Cl_2): ν 3044, 2970, 1578, 1453, 1373, 1242, 752, 702 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 1.67 (s, 3H), 2.12 (s, 3H), 2.27 (s, 3H), 6.79 (s, 1H), 6.86 (d, J = 8.0 Hz, 1H), 7.04 (d, J = 7.6 Hz, 1H), 7.09 (d, J = 6.8 Hz, 1H),, 7.13-7.18 (m, 2H), 7.32 (ddd, J_1 = J_2 = 7.6 Hz, J_3 = 1.2 Hz, 1H), 7.60 (d, J = 7.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 15.9, 20.3, 21.5, 61.7, 120.0, 122.4, 123.1, 125.6, 126.7, 127.7, 128.0, 128.7, 138.4, 139.3, 147.1, 154.5, 187.3; MS (ESI) *m/z*: 236.1 ($M+H^+$, 100); HRMS (ESI) Calcd. for $C_{17}H_{18}N^+$ requires: 236.1434, found: 236.1433.





Compound 4n: 22 mg, 86%, A yellow liquid; IR (CH_2Cl_2): ν 3060, 2971, 1578, 1450, 1374, 1239, 767, 698 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$, TMS): δ 1.68 (s, 3H), 2.11 (s, 3H), 7.00-7.02 (m, 2H), 7.06 (d, *J* = 2.0 Hz, 1H), 7.26-7.31 (m, 4H), 7.51 (d, *J* = 8.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 15.8, 20.1, 62.1, 120.9, 123.0, 125.9, 127.5, 128.0, 129.0, 131.4, 138.5, 148.7, 153.0, 187.7; MS (ESI) *m/z*: 256.1 ($M+H^+$, 100); HRMS (ESI) Calcd. for $C_{16}H_{15}ClN^+$ requires: 256.0888, found: 256.0887.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7.500
7.314
7.308
7.304
7.277
7.273
7.267
7.263
7.258
7.061
7.056
7.023
7.019
7.014
7.003
7.000
2.110
1.679
0.000
Ph
Cl
N
4.03
1.97
1.04
1.02
3.00
2.98
8
7
6
5
4
3
2
1
PPM
187.703
153.014
148.719
138.488
131.364
128.964
128.016
127.470
125.938
122.970
120.936
77.321
77.000
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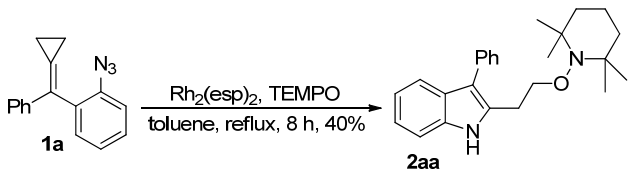
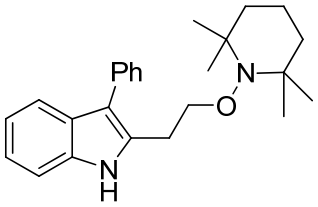
15.833
Ph
Cl
N
200
150
100
50
0PPM

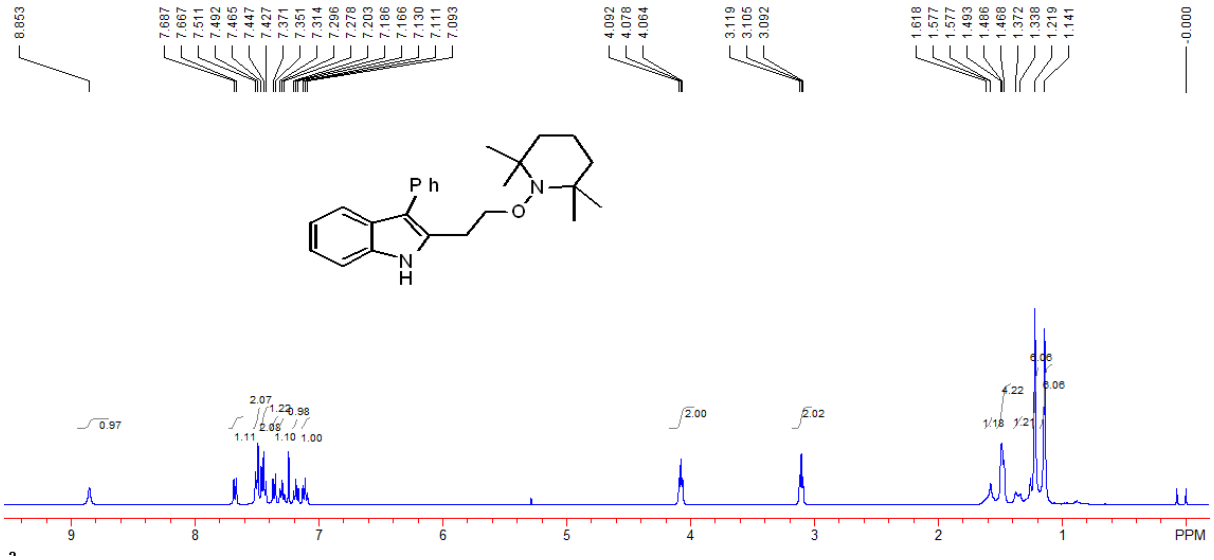
Typical procedure for the synthesis of compound 2aa

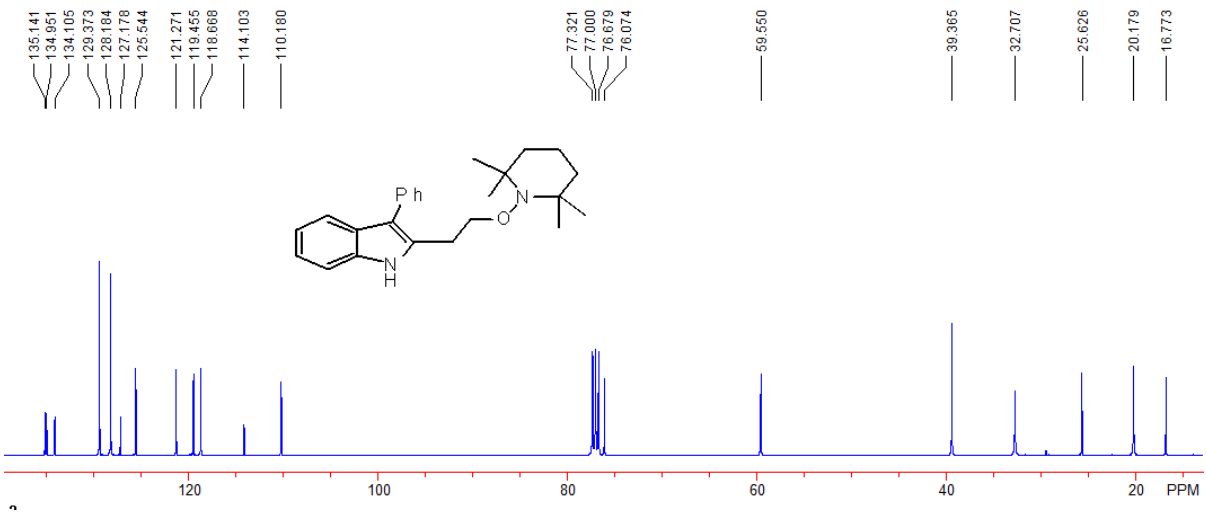


A solution of compound **1a** (0.2 mmol), TEMPO (62.4 mg, 0.4 mmol) and $Rh_2(esp)_2$ (4.5 mg, 0.006 mmol) in dry toluene (1 mL) was stirred at 110 ^oC for 8 h. Then the solvent was removed under reduced pressure and the residue was purified by silica gel flash chromatography (eluent: petroleum ether / ethyl acetate = 30 / 1) to afford the product **2aa** in 40% yield.



Compound 2aa: 30 mg, 40%, A yellow liquid; IR (CH_2Cl_2): ν 3416, 2926, 1602, 1458, 1359, 1045, 741, 701 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$, TMS): δ 1.14 (s, 6H), 1.22 (s, 6H), 1.34-1.37 (m, 1H), 1.47-1.49 (m, 4H), 1.58-1.62 (m, 1H), 3.11 (t, *J* = 5.2 Hz, 2H), 4.08 (t, *J* = 5.2 Hz, 2H), 7.09-7.13 (m, 1H), 7.17-7.20 (m, 1H), 7.28-7.31 (m, 1H), 7.36 (d, 1H, *J* = 8.0 Hz), 7.43-7.47 (m, 2H), 7.50 (d, *J* = 7.6 Hz, 2H), 7.68 (d, *J* = 8.0 Hz, 1H), 8.85 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 16.8, 20.2, 25.6, 32.7, 39.4, 59.6, 76.1, 110.2, 114.1, 118.7, 119.5, 121.3, 125.5, 127.2, 128.2, 129.4, 134.1, 135.0, 135.1; MS (ESI) *m/z*: 377.3 ($M+H^+$, 100); HRMS (ESI) Calcd. for $C_{25}H_{33}N_2O^+$ requires: 377.2587, found: 377.2592.

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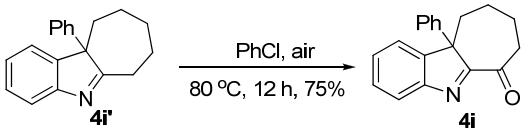
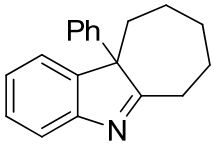
134.105
129.373
128.184
127.178
125.544
121.271
119.455
118.668
114.103
110.180
77.321
77.000
76.679
76.074
59.550
39.365
32.707
25.626
20.179
16.773
Ph
N
O
N
H
120
100
80
60
40
20
PPM

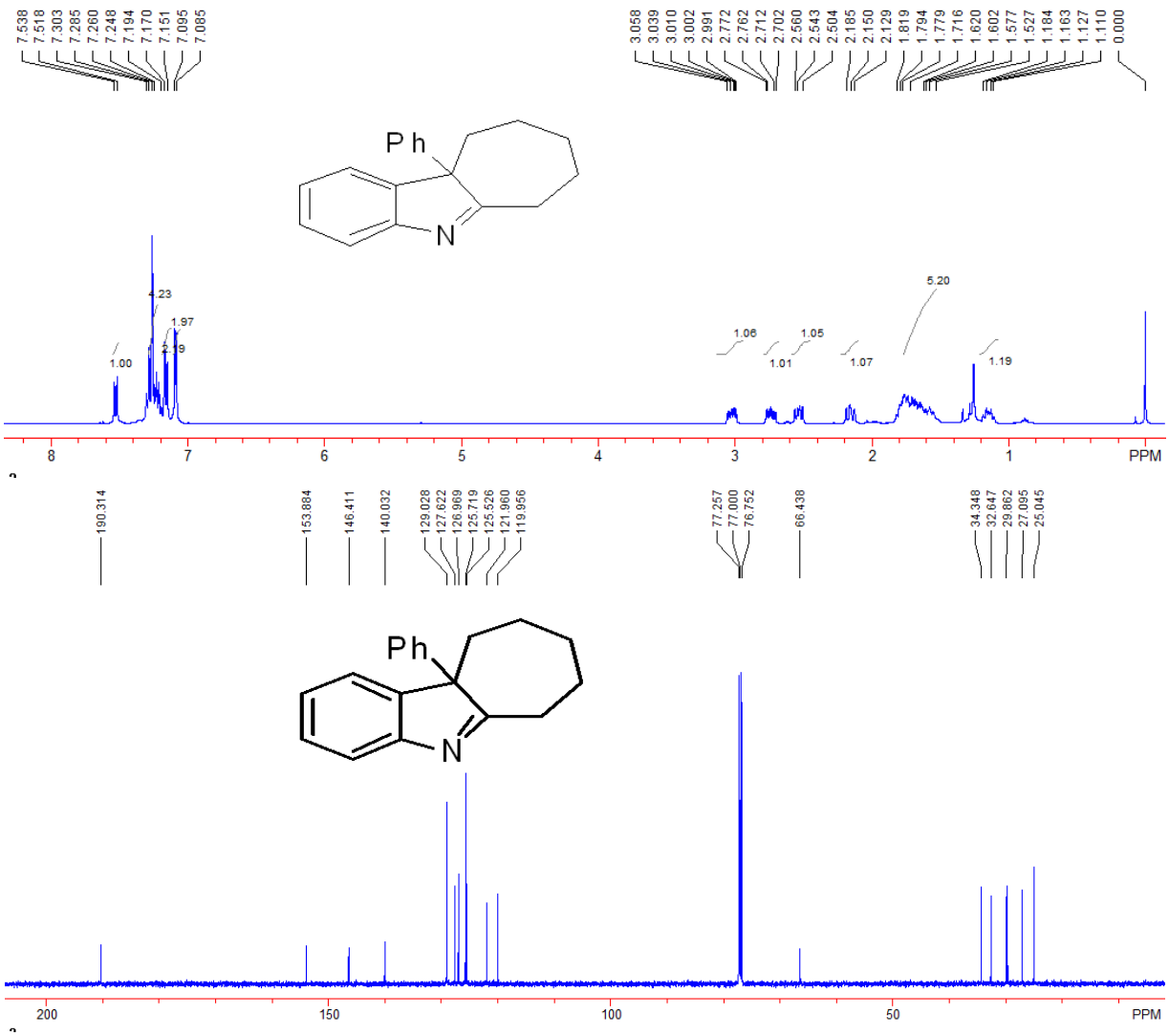
Transformation of compound 4i'



Compound **4i'** (26 mg, 0.1 mmol) was dissolved in dry PhCl (1.0 mL) and the reaction mixture was stirred under air atmosphere at 80 ^{o}C for 12 h. Then the solvent was removed under reduced pressure and the residue was purified by silica gel flash chromatography (eluent: petroleum ether / ethyl acetate = 10 / 1) to afford the product **4i** in 75% yield.



Compound 4i': 24 mg, 48%, A yellow solid, m.p. 110-112 ^{o}C; IR (CH_2Cl_2): ν 3058, 2927, 2853, 1527, 1445, 1078, 754, 701 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 1.11-1.84 (m, 1H), 1.53-1.82 (m, 5H), 2.13-2.19 (m, 1H), 2.50-2.56 (m, 1H), 2.70-2.77 (m, 1H), 2.99-3.06 (m, 1H), 7.09 (d, *J* = 4.0 Hz, 2H), 7.16 (d, *J* = 7.6 Hz, 2H), 7.19-7.30 (m, 4H), 7.53 (d, *J* = 8.0 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$, TMS): δ 25.0, 27.1, 29.9, 32.6, 34.3, 66.4, 120.0, 122.0, 125.5, 125.7, 127.0, 127.6, 129.0, 140.0, 146.4, 153.9, 190.3; MS (EI) m/z (%): 261 (6.2) [M^+], 259 (100.0), 258 (64.4), 248 (19.9), 230 (22.4), 219 (41.9), 218 (33.7), 204 (22.6); HRMS (EI) Calcd. for $C_{19}H_{19}N$ (M^+) requires 261.1517, found: 261.1512.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7.170
7.151
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7.085
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3.010
3.002
2.991
2.772
2.762
2.712
2.702
2.560
2.543
2.504
2.185
2.150
2.129
1.819
1.794
1.779
1.716
1.620
1.602
1.577
1.527
1.184
1.163
1.127
1.110
0.000
Ph
N
1.00
4.23
1.97
2.19
1.06
1.01
1.05
1.07
5.20
1.19
8
7
6
5
4
3
2
1
PPM
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153.884
146.411
140.032
129.028
127.622
126.969
125.719
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121.960
119.956
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77.000
76.752
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Ph
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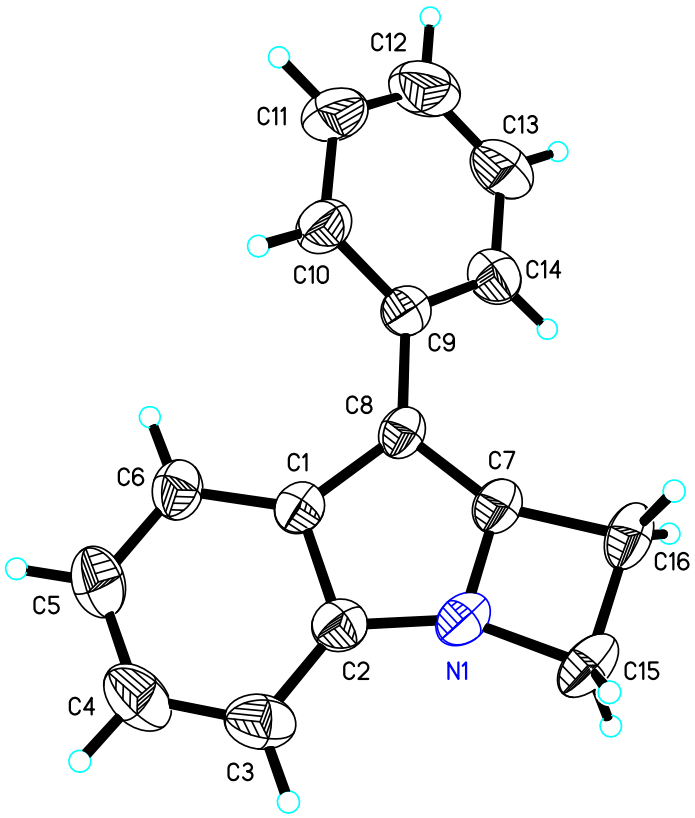
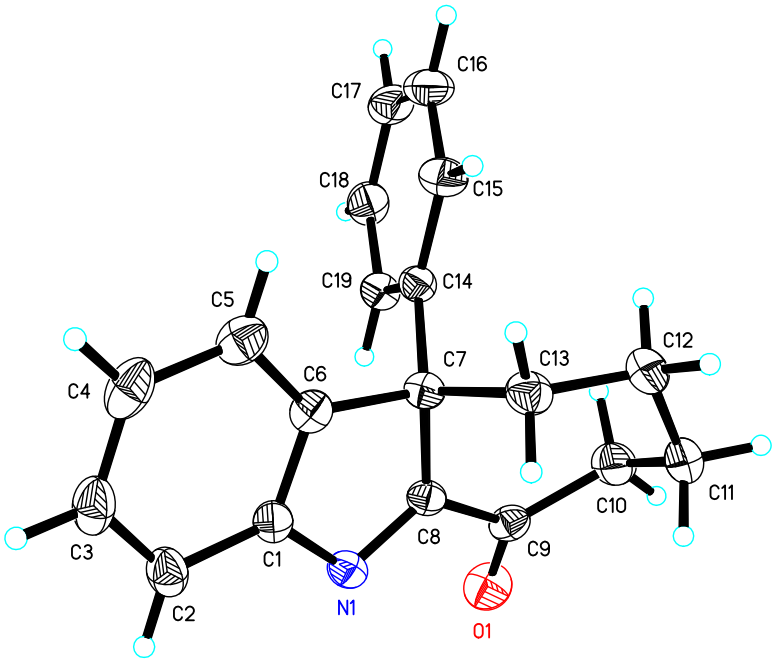
200
150
100
50
PPM

The crystal data of 2a and 4i



The crystal data of **2a** have been deposited in CCDC with number 949600. Empirical Formula: $C_{16}H_{13}N$; Formula Weight: 219.27; Crystal Color, Habit: colorless; Crystal Dimensions: 0.212 x 0.158 x 0.112 mm; Crystal System: Orthorhombic; Lattice Parameters: a = 16.7246(16) A, alpha = 90 deg. b = 7.1468(7) A, beta = 90 deg. c = 20.1020(19) A, gamma = 90 deg.; V = 2402.7(4) $Å^3$; Space group: Pbca; Z = 8; D_{calc} = 1.212 g/cm^3; F_{000} = 928; Diffractometer: Rigaku AFC7R; Residuals: R; R_w: 0.0457, 0.1231.



The crystal data of **4i** have been deposited in CCDC with number 1003610. Empirical Formula: $C_{19}H_{17}NO$; Formula Weight: 275.33; Crystal Color, Habit: colorless; Crystal Dimensions: 0.199 x 0.176 x 0.123 mm; Crystal System: Monoclinic; Lattice Parameters: a = 9.2535(19) A, alpha = 90 deg. b = 14.994(3) A, beta = 101.697(4) deg. c = 10.714(2) A, gamma = 90 deg.; V = 1455.7(5) $Å^3$; Space group: P 21/n; Z = 4; D_{calc} = 1.256 g/cm^3; F_{000} = 584; Diffractometer: Rigaku AFC7R; Residuals: R; R_w: 0.0591, 0.1604.

Computational details

The geometries of all systems have been optimized at BPW91 level. The 6-31G* basis sets were used for C, H, N, O atoms and the 1997 Stuttgart relativistic small-core effective core potential Stuttgart RSC 1997 ECP)20 for Rh, augmented with a 4f function [ζ_f(Rh) = 1.350], which is denoted as BSI composite basis set.[5] The subsequent frequency calculations on the stationary points were carried out at the same level of theory to ascertain the nature of the stationary points as minima or first-order saddle points on the respective potential energy surfaces. All transition states were characterized by one and only one imaginary frequency pertaining to the desired reaction coordinate. The intrinsic reaction coordinate (IRC) calculations were carried out at the same level of theory to further authenticate the transition states. The conformational space of flexible systems has first been searched manually. Thermochemical corrections to 298.15 K have been calculated for all minima from unscaled vibrational frequencies obtained at this same level. In the present computational studies, we employed Rh_2(formate)$_4$ as models for Rh_2(esp)$_2$-catalyzed reactions due to the computational tractability.

The optimized structure of Rh_2-Nitrene intermediate **A'** at BPW91/BSI level is shown in Scheme S1. The Mulliken spin density on nitrogen atom is 1.05, indicating one unpaired electron is localized on the nitrogen atom center. Thus, this intermediate has radical character.

Scheme S1. The optimized structure of Rh_2-nitrene and its character

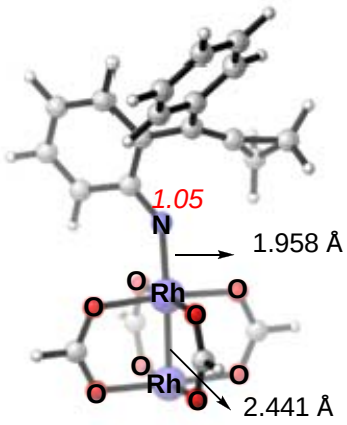


Table S1. The total energies, enthalpies and free energies of all species shown in Scheme 5.

	E_{tot} (E_h)[a]	H_{298}[a]	G_{298}[a]
B1	-1650.199312	-1649.833397	-1649.922602
TS1	-1650.191832	-1649.827468	-1649.91621
C1	-1650.204107	-1649.838771	-1649.930274
D1	-1650.24234	-1649.874327	-1649.963979
TS2	-1650.223023	-1649.85648	-1649.944396
E1	-1650.242862	-1649.874634	-1649.963749
B2	-1689.500877	-1689.104392	-1689.201416
TS3	-1689.483861	-1689.089006	-1689.183865
C2	-1689.507339	-1689.113104	-1689.208157
D2	-1689.538711	-1689.141043	-1689.233024
TS4	-1689.521524	-1689.125494	-1689.215316
E2	-1689.581514	-1689.183002	-1689.274282
B3	-1728.82984	-1728.403553	-1728.496665
TS5	-1728.797688	-1728.374564	-1728.469193
C3	-1728.809578	-1728.385842	-1728.484373
D3	-1728.865528	-1728.437666	-1728.53313
TS6	-1728.839559	-1728.41374	-1728.506052
E3	-1728.899013	-1728.470606	-1728.56288

Archive entries

B1

```
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 164991,-0.026415698,0.1489431334\C,2.5510050036,-0.0073881407,1.333391
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 900525,-0.0508983545\C,-2.6711330971,0.0727903719,1.0796534037\O,-2.16
 38365223,0.0832801594,2.2490126917\H,-3.7748256251,0.10106985,1.027700
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 95645,1.1367776462\O,-0.0988916685,2.1056546851,2.2946459065\H,-0.0615
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TS1

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 8656394378,1.6318356068,1.6834252933\O,-3.8497327627,1.048578635,1.121
 123021\H,-3.1201881188,2.4042937144,2.4317374441\O,-1.1546961673,-1.41
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187749\C,4.6032334625,-0.5558619035,-0.1280670131\C,5.7728708411,-0.00
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890781,-1.4297406892\C,7.1472648852,-1.7707430516,-0.4906370335\H,7.90
49600546,-0.1674980296,0.7599072503\H,6.0931704438,-3.2216176688,-1.71
18938974\H,8.1254691018,-2.2393190739,-0.6290057118\C,2.0412655884,-0.
5739307025,0.3925047538\C,2.096788188,-1.5499639319,2.0309219326\C,1.8
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,1.3232574\PG=C01 [X(C20H17N1O8Rh2)]\\@

C1

1\1\GINC-SHI_03\FOpt\UBPW91\GenECP\C20H17N1O8Rh2(3)\YIN\16-Dec-2014\0\
\#p opt bpw91/genecp\\Title Card Required\\0,3\Rh,0.00830508,-0.004391
2042,-0.0460697116\Rh,-0.043123613,0.0284102533,2.3927507874\O,2.07216
31697,-0.018416016,0.0931494008\C,2.5940544932,-0.0032894067,1.2625481
029\O,2.0077059528,0.024828083,2.3943548898\H,3.6989247155,-0.01651178
38,1.2870863285\O,0.0285237163,-2.0694249219,0.0815931164\C,0.00535519
41,-2.6001934494,1.2466959758\O,-0.0327069116,-2.0218022034,2.38256168
12\H,0.0201212497,-3.7051420533,1.2639063184\O,-2.0635799263,0.0153559
759,0.0150793649\C,-2.6322099123,0.0301682897,1.1620120674\O,-2.091600
8502,0.0311802473,2.3163468558\H,-3.7372001589,0.0433344668,1.14253200
14\O,-0.0170440027,2.0637639678,0.0319753323\C,-0.0435509664,2.6242576
242,1.1820532843\O,-0.0508293489,2.0758404188,2.3338937755\H,-0.061329
507,3.7291914328,1.1694005804\C,0.7244811783,0.9984628868,-2.911276086
5\C,0.2793437287,0.9752603852,-4.2677970935\C,1.7452674384,1.857426003
2,-2.5037600171\C,-0.7726084583,-0.0129151938,-4.3288805353\C,0.835613
1354,1.8598089544,-5.2081981764\C,2.3170499757,2.7174728515,-3.4684876

789\H,2.095988616,1.8621784971,-1.4730195025\C,1.8650839755,2.7268306139,-4.7975904557\H,0.4721879252,1.8787687519,-6.2391735258\H,3.1221124579,3.3927632593,-3.1657296468\H,2.3148008385,3.4125416668,-5.5206717237\N,-0.0155274265,0.0590680339,-2.1542157459\C,-1.5464313204,-0.3831706479,-5.5167803536\C,-0.8950727742,-0.6090424785,-6.7563384889\C,-2.9597497408,-0.4909629878,-5.4776275583\C,-1.6261298787,-0.9460032532,-7.9011989406\H,0.1954732724,-0.5510436069,-6.801114972\C,-3.687354149,-0.8213932948,-6.6261295322\H,-3.4875037257,-0.2670545646,-4.5470159237\C,-3.02482015,-1.0545595231,-7.8421030304\H,-1.1015352418,-1.1299878196,-8.843184137\H,-4.778005002,-0.8861176188,-6.5747918692\H,-3.5951513308,-1.3146262918,-8.7381388211\C,-0.8902349575,-0.5492612577,-3.002737885\C,-0.929427722,-3.0136863741,-2.9667686619\C,-1.6987866589,-1.7731016143,-2.6106347181\H,-0.9694774367,-3.4153055493,-3.9817884909\H,-0.1414310542,-3.364858577,-2.2990208428\H,-1.90571668,-1.7376305846,-1.5330661044\H,-2.6641471196,-1.759808673,-3.1401785163\\Version=EM64L-G09RevA.01\State=3-A\HF=-1650.2041072\S2=2.009104\S2-1=0.\S2A=2.000052\RMSD=3.703e-09\RMSF=1.333e-05\Dipole=-0.2412111,0.0204016,-1.5644025\Quadrupole=4.4839177,-1.7722173,-2.7117004,4.4039848,3.4673869,0.8590316\PG=C01 [X(C20H17N1O8Rh2)]\\@

D1

1\1\GINC-SHI_03\FOpt\RBPW91\GenECP\C20H17N1O8Rh2\YIN\16-Dec-2014\0\\#p opt bpw91/genecp\\Title Card Required\\0,1\Rh,0.0072608312,0.0307556731,0.0835105584\Rh,-0.0484446973,0.2934138857,2.515409341\O,2.0678267617,-0.0873743278,0.2360773848\C,2.5843644802,0.0088203802,1.4039135262\O,1.9994587744,0.1741870825,2.5248637298\H,3.6873900025,-0.0623868775,1.4394794009\O,-0.1045264594,-2.0179598861,0.4047999786\C,-0.1587849834,-2.4325397764,1.6164733687\O,-0.1602715216,-1.750941582,2.6928288099\H,-0.2112038205,-3.5305339384,1.7386250395\O,-2.0647316947,0.1731127918,0.1364323675\C,-2.6325256566,0.3257834797,1.2749710613\O,-2.0962553564,0.4074748366,2.4270270366\H,-3.7358613787,0.396936568,1.2478738834\O,0.1007390284,2.0936449864,-0.0377827229\C,0.1007030596,2.7587022063,1.0562054438\O,0.0592648813,2.3247853487,2.2549160181\H,0.1430287112,3.8576275165,0.9406997726\C,0.8092400794,0.6649441941,-2.8948955108\C,0.4691216198,0.4666436145,-4.3060064491\C,1.8381592998,1.5984880428,-2.5467725251\C,-0.541235471,-0.4909513895,-4.3514199124\C,1.1306928877,1.2249231496,-5.324617957\C,2.4593794682,2.2940888558,-3.5627363898\H,2.1147031492,1.7395813568,-1.5038496197\C,2.1061989171,2.1205302835,-4.9476353874\H,0.8547791794,1.0886438491,-6.3734479111\H,3.2492040332,3.0088021289,-3.3131076989\H,2.6276203945,2.7136215815,-5.7039361149\N,0.0686763146,-0.113704685,-2.085263742\C,-1.2074342596,-1.0361405371,-5.5478858465\C,-0.4481442557,-1.6489043531,-6.5728149701\C,-2.6084644955,-0.9327526382,-5.7192953607\C,-1.0719289653,-2.1535041023,-7.7216718403\H,0.6345002174,-1.7397854703,-6.4499765864\C,-3.2279756932,-1.4355131756,-6.8706783629\H,-3.2053655388,-0.4146920797,-4.9641026029\C,-2.4633431287,-2.051602444,-7.8732474413\H,-0.4689073179,-2.6301795063,

-8.4997140869\H,-4.3106485166,-1.3356605406,-6.989349909\H,-2.94893117
42,-2.4448755868,-8.7706394065\C,-0.7622807198,-0.8974872167,-2.952591
2732\C,-0.8388298406,-2.4501143958,-2.665937568\C,-2.0266741947,-1.606
9938294,-2.433075104\H,-0.7930228631,-3.076845651,-3.5594637061\H,-0.2
425393064,-2.7614946817,-1.8081187796\H,-2.2910507792,-1.3365815528,-1
.4110090714\H,-2.8552937047,-1.6668012089,-3.1404687333\\Version=EM64L
-G09RevA.01\State=1-A\HF=-1650.2423401\RMSD=4.196e-09\RMSF=1.748e-05\D
ipole=-0.3516092,-0.5950718,-2.5175818\Quadrupole=3.9343044,0.0879265,
-4.0222309,5.0961941,2.7447795,2.9456798\PG=C01 [X(C20H17N1O8Rh2)]\\@

TS2

1\1\GINC-SHI_02\FTS\RBPW91\GenECP\C20H17N1O8Rh2\YIN\19-Dec-2014\0\\#p
opt=(calcfc,ts,noeigen) geom=check bpw91/genecp\\rh2och4_3m_ts1\\0,1\R
h,0.0229131474,-0.0275973244,-0.009707054\Rh,-0.0469860568,0.043383781
6,2.4310121543\O,2.0911346414,-0.0124665496,0.1380049935\C,2.599864263
4,0.0283727077,1.3125403019\O,2.0064925157,0.0674892114,2.4405591699\H
,3.7053698852,0.0304346732,1.3488004914\O,0.0408207985,-2.1048493308,0
.1456446386\C,0.0178711062,-2.610569815,1.3237596847\O,-0.0187987615,-
2.0121524609,2.4471361058\H,0.0330449242,-3.7159832105,1.3651160972\O,
-2.0491047554,-0.0518441967,0.0178063333\C,-2.6268173613,-0.019140486,
1.1607310043\O,-2.1015570081,0.0164068028,2.3215826648\H,-3.7327037043
,-0.0243321795,1.1314382874\O,-0.0003641384,2.0373504554,0.0157811485\
C,-0.0437698914,2.6178812806,1.1559288617\O,-0.0704772823,2.0951012021
,2.319146495\H,-0.0600490697,3.7231530456,1.1221583384\C,0.8161072157,
0.7405316424,-3.0205948634\C,0.445890635,0.5522010109,-4.3972037457\C,
1.8807947935,1.6047904543,-2.6806649985\C,-0.6866537479,-0.3318379238,
-4.3928251968\C,1.1071053484,1.2676583375,-5.4235398356\C,2.5352518914
,2.2721193689,-3.7132463085\H,2.1715431636,1.7314929308,-1.6386175168\
C,2.1513863829,2.1169247773,-5.0728588806\H,0.796401721,1.160895451,-6
.4660921\H,3.3646217565,2.9431991159,-3.4709848366\H,2.6824150497,2.67
56698239,-5.8481292929\N,0.0108816896,-0.0066593955,-2.1744363394\C,-1
.6498071305,-0.5196532676,-5.5005019122\C,-1.2118016645,-0.9226197868,
-6.782676331\C,-3.0264750399,-0.2720937846,-5.3007800911\C,-2.12528565
92,-1.0694901624,-7.8343843707\H,-0.151159129,-1.134166106,-6.94565874
68\C,-3.9374789681,-0.4221207555,-6.3551217344\H,-3.3726585212,0.06593
27599,-4.3201818847\C,-3.4908860203,-0.8207638474,-7.6240696303\H,-1.7
703176287,-1.3834650984,-8.8200045634\H,-4.9985368419,-0.2188688996,-6
.1853357039\H,-4.2028070842,-0.9359733751,-8.4459376844\C,-0.912552115
2,-0.6207538371,-2.9636104537\C,-0.5042093365,-2.2871934568,-3.5959871
874\C,-1.5851800062,-1.9148492696,-2.6288168285\H,-0.7590715214,-2.708
8359329,-4.5705715465\H,0.4935847873,-2.4942856678,-3.2036004573\H,-1.
4384218087,-2.2168326725,-1.5888533974\H,-2.6085228211,-2.0458507271,-
2.9955118266\\Version=EM64L-G09RevA.01\State=1-A\HF=-1650.2230226\RMSD
=3.907e-09\RMSF=5.692e-06\Dipole=-0.56863,-0.810636,-2.963073\Quadrupo
le=4.0329941,-0.7476661,-3.2853281,4.4334564,4.6275231,4.6661784\PG=C0
1 [X(C20H17N1O8Rh2)]\\@

E1

1\1\GINC-SHI_02\FOpt\RBPW91\GenECP\C20H17N1O8Rh2\YIN\24-Dec-2014\0\\#p
opt bpw91/genecp\\rh2och4_3m_ts1\\0,1\Rh,0.0131121049,-0.0042114126,-
0.0181672132\Rh,-0.0115013205,0.0143423545,2.4208877124\O,2.082327285,
0.0010398491,0.0908996133\C,2.6138878633,0.002659384,1.2558682146\O,2.
0419785904,0.0131340346,2.3955373291\H,3.7196977743,-0.0050659844,1.27
05075232\O,0.03362181,-2.0782644825,0.0936719187\C,0.017693378,-2.6117
51061,1.2587965727\O,-0.0059163668,-2.0404828072,2.3971441603\H,0.0271
779055,-3.7177436565,1.2729887943\O,-2.0549915496,-0.0266372096,0.0384
778972\C,-2.613680513,-0.0083144706,1.1910277056\O,-2.0675905097,0.012
8562636,2.3427416871\H,-3.7196040662,-0.0122515976,1.1800370369\O,-0.0
03431723,2.065152671,0.0516987317\C,-0.013280976,2.6181400818,1.206955
9685\O,-0.0150136602,2.0665223325,2.3562712367\H,-0.0219217287,3.72398
97241,1.2008215819\C,0.8327792409,0.6933146374,-3.0589290609\C,0.61637
8755,0.2739565508,-4.3997664607\C,1.8315431272,1.6179854916,-2.7316898
188\C,-0.596189861,-0.6230519234,-4.3878327018\C,1.3789639723,0.818261
9938,-5.4362835\C,2.6150880183,2.1256572342,-3.7796363477\H,1.98453650
48,1.9258416966,-1.697982305\C,2.3954894334,1.733757334,-5.113470962\H
,1.1933237065,0.5350748479,-6.4759638644\H,3.4062787288,2.8461008831,-
3.5540627929\H,3.0211670604,2.1481955088,-5.9087536283\N,-0.0621677961
,0.0251226743,-2.1639956559\C,-1.6658887797,-0.2764227236,-5.410336390
4\C,-1.6390801045,-0.8547195364,-6.6943790139\C,-2.6726809573,0.660815
593,-5.1075157283\C,-2.6001002778,-0.5060679816,-7.6546051448\H,-0.861
4022249,-1.5825154496,-6.9470378147\C,-3.6378633771,1.0034149252,-6.06
50327472\H,-2.6979299988,1.1208516574,-4.1152213593\C,-3.6046383205,0.
4217924347,-7.3412924811\H,-2.5647702795,-0.9637683176,-8.6474047246\H
,-4.4179992544,1.7267254349,-5.8112107076\H,-4.3578171573,0.6890427264
,-8.0876856695\C,-0.9302829373,-0.6211909759,-2.9064316457\C,-0.536477
2068,-2.2072700559,-4.0767161618\C,-1.4555154664,-2.0267388175,-2.8156
331046\H,-0.9462612137,-2.8232009024,-4.8899662192\H,0.4776758818,-2.5
263097037,-3.8024371809\H,-1.2090013835,-2.5789907417,-1.9026361411\H,
-2.5202855789,-2.1228879009,-3.0743614359\\Version=EM64L-G09RevA.01\St
ate=1-A\HF=-1650.2428621\RMSD=5.490e-09\RMSF=1.168e-05\Dipole=-0.28683
38,-0.4028102,-2.6074422\Quadrupole=3.0002768,1.9283817,-4.9286584,2.3
663331,2.4213158,3.2379088\PG=C01 [X(C20H17N1O8Rh2)]\\@

B2

1\1\GINC-SHI_03\FOpt\UBPW91\GenECP\C21H19N1O8Rh2(3)\YIN\17-Dec-2014\0\
\#p opt bpw91/genecp\\Title Card Required\\0,3\Rh,-0.0060398689,0.0058
932892,-0.1116988945\Rh,0.0537826819,-0.0325625358,2.3184975542\O,2.09
71821459,-0.0741388894,-0.0551378556\C,2.6556109134,-0.0926330168,1.09
07241022\O,2.1048648932,-0.0707548031,2.2450322053\H,3.7612319238,-0.1
318478963,1.0924511481\O,-0.0865202584,-2.3712420968,0.2115784795\C,-0
.0372713063,-2.774710594,1.4021584061\O,0.034482548,-2.0568174572,2.46
96777651\H,-0.0535102342,-3.8662107534,1.5964692885\O,-2.1135695486,0.

0950428454,0.0676698036\C,-2.609709171,0.057467242,1.2414502831\O,-1.9
966725592,-0.0085886294,2.3615192525\H,-3.7137888099,0.0871696072,1.30
60920519\O,0.0548250207,2.3446312317,0.2209613958\C,0.0670347864,2.729
1138493,1.4198670262\O,0.0748382012,1.995376229,2.4790489364\H,0.07306
66166,3.8180641309,1.6274726884\C,0.85752372,0.8908189137,-2.936990879
3\C,0.7606242865,0.6494016643,-4.3784259096\C,1.7251701849,1.922955302
2,-2.4516138751\C,-0.1632375904,-0.3706894134,-4.5659745668\C,1.522769
6848,1.4429893725,-5.2987254168\C,2.4469959735,2.6496731385,-3.3742333
699\H,1.7805927137,2.1281609072,-1.3842945363\C,2.3506961145,2.4189122
782,-4.7936458869\H,1.423039485,1.2790789015,-6.374351488\H,3.11042060
7,3.4450298043,-3.0220887404\H,2.9366827768,3.0460174645,-5.4707940327
\N,0.0626834851,0.0683961586,-2.2368494233\C,-0.4747585897,-1.00645797
17,-5.8570794848\C,0.5917949719,-1.4454568201,-6.6820382715\C,-1.79789
50753,-1.1808427763,-6.3294256315\C,0.3430839584,-2.0444276275,-7.9228
986121\H,1.618750311,-1.3386894402,-6.3230080547\C,-2.0413092012,-1.76
82450956,-7.5769575069\H,-2.6384333636,-0.8215855963,-5.733208842\C,-0
.9745823425,-2.2066310496,-8.3767523175\H,1.1819220374,-2.3885800913,-
8.5343805616\H,-3.071169384,-1.8797674893,-7.927444476\H,-1.1694786443
,-2.6711728691,-9.3471570417\C,-0.6380991692,-0.7937305708,-3.19663934
62\C,-2.186219445,-0.9974536152,-2.9658432857\C,-0.508697973,-2.368075
4482,-2.9775318841\C,-2.0365433462,-2.524134808,-3.1823453946\H,-2.851
7308758,-0.4206238904,-3.6250686707\H,-2.414275399,-0.745259984,-1.923
0225678\H,0.1643685779,-2.8814024495,-3.6798191209\H,-0.2023190004,-2.
5646087476,-1.9430446911\H,-2.2986869973,-2.8449316054,-4.2011874481\H
,-2.5570169898,-3.1702467224,-2.4600504411\\Version=EM64L-G09RevA.01\S
tate=3-A\HF=-1689.5008767\S2=2.007184\S2-1=0.\S2A=2.000029\RMSD=6.597e
-09\RMSF=5.368e-06\Dipole=0.0398975,-0.1957606,-3.3307491\Quadrupole=2
.4771365,-2.6430783,0.1659418,6.0852169,-0.4925331,3.7745353\PG=C01 [X
(C21H19N1O8Rh2)]\\@

TS3

1\1\GINC-SHI_03\FTS\UBPW91\GenECP\C21H19N1O8Rh2(3)\YIN\18-Dec-2014\0\\
#p opt=(calcfc,ts,noeigen) genecp bpw91\\Title Card Required\\0,3\Rh,-
1.122270952,0.0577736434,-0.2258633448\Rh,-3.4903974431,-0.4131133331,
-0.0097401633\O,-1.3310749648,1.3286115455,1.442812507\C,-2.4968001492
,1.4525310531,1.9421308894\O,-3.5847408238,0.8888203556,1.5729540105\H
,-2.5868496274,2.1349628488,2.8083908216\O,-0.9481522993,-1.7913083714
,1.3275726198\C,-2.0476058995,-2.3070733583,1.6613295565\O,-3.22958741
76,-1.9662852372,1.2808459508\H,-2.0399619799,-3.1621154785,2.36898032
72\O,-1.1104736487,-1.2745045273,-1.8586914415\C,-2.2155400083,-1.8323
166203,-2.1654336917\O,-3.355911617,-1.7023686282,-1.6006920173\H,-2.1
904642781,-2.521723242,-3.0304799169\O,-1.8705508922,1.8002237214,-1.6
110343718\C,-3.1154494453,1.8498193313,-1.793852167\O,-4.0183983371,1.
0841310968,-1.2835788853\H,-3.5203033532,2.6330936915,-2.4659991148\C,
1.5552415382,1.6579238602,-0.0564852813\C,2.9707791614,1.5248544114,0.
1512217801\C,0.9453140819,2.9322596054,-0.0388226499\C,3.2723509016,0.

1328993679,0.0027721552\C,3.7807006089,2.6697608994,0.3492901948\C,1.7
627751819,4.0397075792,0.1734626892\H,-0.1257174202,3.0307520568,-0.21
4415497\C,3.1669097548,3.9173330742,0.3640483094\H,4.8634106665,2.5741
133141,0.4637573499\H,1.314247672,5.0373734291,0.1780920524\H,3.768826
7693,4.8182105592,0.509409723\N,0.9659038809,0.427595644,-0.2836035994
\C,4.6255612285,-0.4417704848,-0.1409085934\C,5.6288766345,-0.16893711
43,0.8180374036\C,4.9614839068,-1.2267374105,-1.2670472958\C,6.9240642
214,-0.6779124804,0.6609430583\H,5.3837589584,0.4339414133,1.697069861
1\C,6.2602546707,-1.7274445705,-1.4249988128\H,4.2080224161,-1.4175385
628,-2.0347039305\C,7.2435870374,-1.4592707874,-0.4605626889\H,7.68517
34413,-0.4644478755,1.4165178811\H,6.5049931935,-2.3257040482,-2.30692
33135\H,8.2554496858,-1.8548564667,-0.5833976009\C,1.9704268069,-0.517
3730827,-0.2115887818\C,1.7592380045,-2.0092571013,-0.449939559\C,2.37
73919699,-1.1209824009,1.5531615482\C,2.4003765105,-2.4896474964,0.874
8602885\H,2.2134032244,-2.3880120094,-1.377902542\H,0.6827957234,-2.21
16408082,-0.4787758098\H,3.2286075746,-0.807765924,2.1684122914\H,1.41
55351196,-0.8251935202,1.987325749\H,3.4272009523,-2.8595334702,0.7419
388903\H,1.815730059,-3.2469920911,1.4193641618\\Version=EM64L-G09RevA
.01\State=3-A\HF=-1689.4838607\S2=2.005356\S2-1=0.\S2A=2.000015\RMSD=5
.215e-09\RMSF=4.959e-06\Dipole=3.7158684,-0.3350537,0.4610321\Quadrupo
le=2.3460392,2.1828183,-4.5288575,-7.4676366,3.2252986,3.7810101\PG=C0
1 [X(C21H19N1O8Rh2)]\\@

C2

1\1\GINC-SHI_02\FOpt\UBPW91\GenECP\C21H19N1O8Rh2(3)\YIN\17-Dec-2014\0\
\#p opt bpw91/genecp\\Title Card Required\\0,3\Rh,0.0512531305,0.02964
53437,-0.0388327562\Rh,-0.4492781901,0.3779351321,2.3240843594\O,2.055
2850194,0.1530559789,0.4694064145\C,2.3507796571,0.3585120373,1.698443
1832\O,1.5647642873,0.5048462899,2.6915176973\H,3.4318070498,0.4157519
454,1.921483336\O,0.1104951111,-1.9988924533,0.3803652536\C,-0.1056747
857,-2.3715465705,1.5865676831\O,-0.3660029911,-1.6505611004,2.6052123
212\H,-0.0592369987,-3.4618625339,1.7610747751\O,-1.9950842794,-0.0616
688116,-0.3510858813\C,-2.7647485133,0.0603291797,0.6640304527\O,-2.44
72313127,0.2376518763,1.8861609892\H,-3.8471042143,0.0031366723,0.4471
18167\O,-0.0462537525,2.0848234596,-0.2526358933\C,-0.3071584711,2.788
6590343,0.7836823702\O,-0.5172399191,2.3963079807,1.9793039618\H,-0.35
428009,3.8797584015,0.6144389345\C,1.2694082536,0.7017744913,-2.828956
5068\C,1.0659702987,0.5287650409,-4.2306601936\C,2.2012729489,1.619716
6911,-2.345443835\C,0.0447705422,-0.4833715231,-4.3659706405\C,1.77359
17406,1.323862023,-5.150165516\C,2.9294682092,2.3862749185,-3.28269286
08\H,2.3685722343,1.7366644657,-1.2761908589\C,2.7142376542,2.24899562
76,-4.663573268\H,1.5915793311,1.2316466957,-6.2241066821\H,3.66895590
11,3.1051968704,-2.9190925795\H,3.2800450296,2.8659278394,-5.366790585
8\N,0.4127244837,-0.1708100436,-2.1147613514\C,-0.5187916958,-0.969369
7624,-5.6280516753\C,0.3266535833,-1.2587417461,-6.730148758\C,-1.9174
048323,-1.1244547281,-5.8039224924\C,-0.2049625096,-1.6944988893,-7.94

90968002\H,1.4090358119,-1.1737769097,-6.6056918604\C,-2.4451909649,-1
.5513188273,-7.0271187947\H,-2.5910028935,-0.865950082,-4.9836377138\C
,-1.5926665574,-1.8412087809,-8.104898706\H,0.4673760474,-1.9259017769
,-8.7802454989\H,-3.5283793453,-1.6493417122,-7.1433132946\H,-2.007177
6484,-2.1774467103,-9.0592928842\C,-0.2952328533,-0.888662059,-3.02843
23215\C,-1.1906771352,-2.0380835275,-2.6445732533\C,0.6418032889,-3.81
9287158,-2.6956365155\C,-0.7031894137,-3.4078119814,-3.1959618719\H,-2
.2204447435,-1.8593253943,-2.9982555346\H,-1.2414875348,-2.093197483,-
1.5503656306\H,1.2472325227,-4.5380165152,-3.2525292755\H,0.9839888486
,-3.5145278399,-1.7047908981\H,-0.7153789804,-3.3981089534,-4.30022288
3\H,-1.4742081579,-4.1593218209,-2.9072810361\\Version=EM64L-G09RevA.0
1\State=3-A\HF=-1689.5073387\S2=2.008985\S2-1=0.\S2A=2.000051\RMSD=5.5
06e-09\RMSF=9.161e-06\Dipole=-0.0841319,-0.2720705,-1.6401807\Quadrupo
le=2.9121005,-0.8508396,-2.0612609,5.8614541,4.544983,1.2042141\PG=C01
[X(C21H19N1O8Rh2)]\\@

D2

1\1\GINC-SHI_03\FOpt\RBPW91\GenECP\C21H19N1O8Rh2\YIN\16-Dec-2014\0\\#p
opt bpw91/genecp\\Title Card Required\\0,1\Rh,-0.0227628837,0.0733501
704,0.0241081742\Rh,0.1259610662,0.0407338249,2.4692101401\O,2.0405674
797,-0.0760755227,-0.0100368272\C,2.6541051858,-0.1250426627,1.1132540
11\O,2.1674613572,-0.0884260516,2.2912606505\H,3.7547044189,-0.2095937
362,1.046245832\O,-0.1481610474,-1.9970317499,0.13240003\C,-0.10358467
86,-2.5549263984,1.2844795657\O,0.0066153704,-2.0077078988,2.429018481
6\H,-0.1695833426,-3.658841679,1.2788615213\O,-2.0812617621,0.23211412
45,0.2711193761\C,-2.5499016823,0.2387225726,1.4631000442\O,-1.9201301
165,0.1648584287,2.5689284821\H,-3.6502154874,0.3214902367,1.537949678
\O,0.0842969111,2.1387820798,0.1472445757\C,0.178339537,2.6651836513,1
.3106829714\O,0.230499415,2.0879602431,2.4462687763\H,0.2194356168,3.7
70193951,1.3268214969\C,0.7298986827,0.929864763,-2.90091774\C,0.50039
92693,0.7370336314,-4.340221586\C,1.710496875,1.8916082049,-2.47622667
9\C,-0.4835130314,-0.227382816,-4.4755090265\C,1.2298586987,1.51261545
61,-5.3043921737\C,2.3920056057,2.6000801368,-3.4393509706\H,1.8950846
29,2.0459462962,-1.4157599868\C,2.1546805424,2.4222855287,-4.852252649
7\H,1.0340072974,1.3783676872,-6.3710990631\H,3.1413066075,3.334454292
7,-3.1287963116\H,2.7211416355,3.0304081379,-5.5627494265\N,-0.0423446
748,0.1327276438,-2.1571619404\C,-0.9448319356,-0.8101686081,-5.748866
8062\C,0.0114411456,-1.3221356787,-6.6612527196\C,-2.3107217283,-0.867
8200074,-6.1149749511\C,-0.3842825829,-1.8806577568,-7.8832713184\H,1.
0697035775,-1.3008052852,-6.3874650493\C,-2.7020381048,-1.4183473693,-
7.3419509727\H,-3.0674342794,-0.4495144643,-5.4483106793\C,-1.74291167
36,-1.931326025,-8.229037717\H,0.3718700676,-2.2816211757,-8.564314159
4\H,-3.7626838014,-1.4421442971,-7.6078199898\H,-2.052831277,-2.366515
1596,-9.1831075242\C,-0.831678938,-0.6919118068,-3.0788930895\C,-2.339
6853432,-0.9506338378,-2.718265702\C,-0.6422626932,-2.2759735706,-2.96
19532173\C,-2.1789998754,-2.457445184,-3.0411922073\H,-3.0806697123,-0

.3594969909,-3.2764072354\H,-2.4780975948,-0.7659966702,-1.6465578438\
H,-0.0233318056,-2.7334891928,-3.7473614998\H,-0.2414497623,-2.5122410
94,-1.9709132328\H,-2.5223566854,-2.7191652751,-4.0525963238\H,-2.6228
308097,-3.1615742387,-2.3212480288\\Version=EM64L-G09RevA.01\State=1-A
\HF=-1689.5387114\RMSD=3.796e-09\RMSF=1.497e-05\Dipole=-0.1557059,-0.2
506852,-2.5747338\Quadrupole=3.6191063,0.0548351,-3.6739414,5.0838183,
-0.0234694,3.2195399\PG=C01 [X(C21H19N1O8Rh2)]\\@

TS4

1\1\GINC-SHI_03\FTS\RBPW91\GenECP\C21H19N1O8Rh2\YIN\22-Dec-2014\0\\#p
opt=(calcfc,ts,noeigen) genecp bpw91\\Title Card Required\\0,1\Rh,-1.1
641602453,0.0686787667,0.1602053566\Rh,-3.5727429713,-0.3206581065,-0.
0035562529\O,-1.5961395149,1.6191472689,1.4644082388\C,-2.8282097409,1
.8470473932,1.7295470008\O,-3.8649056763,1.2464751747,1.293384606\H,-3
.013060563,2.6795491027,2.4341139507\O,-1.1614198399,-1.2303407036,1.7
863332398\C,-2.2807095995,-1.7525962459,2.1300898931\O,-3.4301803673,-
1.596618306,1.6038597394\H,-2.2374905264,-2.4306439204,3.0033440095\O,
-0.9124404329,-1.5177252283,-1.1539817798\C,-1.9656782266,-2.108721480
5,-1.5790535154\O,-3.1855604941,-1.8687080063,-1.2980135204\H,-1.78861
95383,-2.9411707866,-2.2858744629\O,-1.3531939566,1.3315370125,-1.4665
639738\C,-2.5203928683,1.4875751885,-1.9683377925\O,-3.6256259468,0.96
91465786,-1.5985592056\H,-2.5725305899,2.1659200689,-2.8402414923\C,1.
5852719789,1.6529349566,0.0333150406\C,3.0186319441,1.5136129143,-0.05
25234827\C,0.9950463404,2.9389453645,-0.0422043735\C,3.294003028,0.119
3561077,0.0515408874\C,3.8428272285,2.646128941,-0.2795690242\C,1.8298
742206,4.0316402135,-0.2462182426\H,-0.0837056104,3.0528971775,0.05144
78694\C,3.2417600273,3.8931930082,-0.3776154888\H,4.9243953134,2.53308
80752,-0.3901878599\H,1.3892435468,5.0305001227,-0.3183478826\H,3.8533
392366,4.7812925907,-0.5578411276\N,0.9715363575,0.4324038727,0.200363
0826\C,4.5810354366,-0.53836069,-0.2457522615\C,5.7801943627,-0.096021
111,0.3609415116\C,4.6514452588,-1.5850307761,-1.1941078861\C,7.007251
1164,-0.6871789125,0.0342294261\H,5.7434145532,0.7082980392,1.10103187
21\C,5.8807713338,-2.1706036166,-1.5222468909\H,3.7399312805,-1.914735
7505,-1.6979362318\C,7.0616949177,-1.726736861,-0.9074047776\H,7.92349
11393,-0.3358475558,0.5169704668\H,5.9163417677,-2.9721354838,-2.26535
78607\H,8.0202900517,-2.1864042556,-1.1631660019\C,1.9750875104,-0.507
7036853,0.2891147385\C,1.7331974502,-2.00577623,0.4668055495\C,2.75322
66167,-0.6926030494,2.0149975925\C,2.6568273083,-2.1839290332,1.696026
2342\H,1.9661129399,-2.6187116445,-0.4161949271\H,0.6805128145,-2.1586
675834,0.7283236603\H,3.7126507007,-0.2781172306,2.345213307\H,1.90951
10255,-0.2620592872,2.5668293482\H,3.6396634977,-2.6000133854,1.431579
7186\H,2.2335804043,-2.7851050124,2.5168969745\\Version=EM64L-G09RevA.
01\State=1-A\HF=-1689.5215237\RMSD=7.125e-09\RMSF=1.381e-05\Dipole=3.2
082158,-0.3965071,0.432295\Quadrupole=-0.9111429,3.953071,-3.041928,-7
.078739,0.7343312,0.7934405\PG=C01 [X(C21H19N1O8Rh2)]\\@

E2

1\1\GINC-SHI_03\FOpt\RBPW91\GenECP\C21H19N1O8Rh2\YIN\24-Dec-2014\0\\#p
opt genecp bpw91 geom=check\\Title Card Required\\0,1\Rh,1.126119619,
0.0639281435,-0.0681098629\Rh,3.5094179417,-0.3243894192,0.282566134\O
,1.6454032411,1.860079762,-0.9615578722\C,2.8908715655,2.1470526804,-1
.0399163792\O,3.892884789,1.4756584849,-0.626293921\H,3.1238472827,3.1
09170136,-1.5328170845\O,1.3435535346,-0.8766163263,-1.9079552966\C,2.
5073078605,-1.3133217721,-2.2200426061\O,3.5876518922,-1.253405948,-1.
5477054928\H,2.5783354739,-1.807077177,-3.2071706116\O,0.776911257,-1.
7625147547,0.8418973508\C,1.7955809513,-2.4222759606,1.2526074983\O,3.
0299161418,-2.1147295832,1.1748836055\H,1.5676969047,-3.3891348814,1.7
389822251\O,1.0945643159,0.9808008476,1.7881223983\C,2.1970280059,1.04
72118418,2.4368250641\O,3.3494310232,0.6194825581,2.0985710705\H,2.134
9548586,1.5436417611,3.4230266699\C,-1.6948481554,1.6054703799,-0.1557
862707\C,-3.0565362017,1.4653508199,-0.5179205755\C,-1.1684250386,2.82
79184353,0.2697988407\C,-3.2881934909,0.001399588,-0.8428157701\C,-3.9
183823002,2.5591906814,-0.4381510074\C,-2.0424783408,3.9273500446,0.32
69626124\H,-0.1188936702,2.9156387472,0.5463503835\C,-3.3968907445,3.7
993571425,-0.0239746004\H,-4.9781150967,2.4594545971,-0.6885979961\H,-
1.6593512079,4.8972364021,0.6560716159\H,-4.0553341901,4.6707913579,0.
0290268702\N,-0.9915887349,0.3615779439,-0.3249578797\C,-4.3071128814,
-0.6327632528,0.1227177309\C,-5.68311843,-0.6274261964,-0.1795302058\C
,-3.8934002453,-1.1754097351,1.3557827512\C,-6.61823974,-1.1586548217,
0.7207909637\H,-6.0370920544,-0.2020763809,-1.1228452934\C,-4.82725844
21,-1.7101999842,2.2545797418\H,-2.831386564,-1.1765991393,1.618987122
9\C,-6.1938975104,-1.7064569839,1.9399391972\H,-7.6817051708,-1.144384
0411,0.4648992814\H,-4.4823698219,-2.1307462173,3.2035418421\H,-6.9227
827428,-2.1251556154,2.6393699105\C,-1.8696092529,-0.5378319045,-0.684
3559595\C,-1.6995219772,-1.8741497654,-1.3457793434\C,-3.4943798702,-0
.4586649072,-2.3219031325\C,-2.9154827725,-1.903287493,-2.3317432197\H
,-1.7385482843,-2.6986375406,-0.6143729487\H,-0.7247476845,-1.92893521
85,-1.8487998483\H,-4.5430873752,-0.4134164867,-2.6517561129\H,-2.9071
495782,0.2004571891,-2.9839468797\H,-3.679545364,-2.6118471685,-1.9750
995803\H,-2.6184711536,-2.2177161978,-3.3439899383\\Version=EM64L-G09R
evA.01\State=1-A\HF=-1689.5815142\RMSD=7.714e-09\RMSF=8.258e-06\Dipole
=-2.4527075,-0.0934488,-0.4341755\Quadrupole=-4.7608114,3.8536655,0.90
71459,3.9645691,0.4981721,0.8477717\PG=C01 [X(C21H19N1O8Rh2)]\\@

B3

1\1\GINC-SHI_02\FOpt\UBPW91\GenECP\C22H21N1O8Rh2(3)\YIN\25-Dec-2014\0\
\#p geom=check opt genecp bpw91\\Title Card Required\\0,3\Rh,-1.065478
3006,-0.0210127904,0.1211361477\Rh,-3.415922264,-0.3236741249,0.740838
2083\O,-1.1277964111,1.7418814301,1.207507322\C,-2.230917601,2.0744710
117,1.7647809459\O,-3.3487060583,1.4610433419,1.7451483042\H,-2.204314
1693,3.0203248674,2.3359318995\O,-0.6073545352,-0.9881152492,1.8970162
124\C,-1.5668525038,-1.3908349736,2.6429659155\O,-2.8223640764,-1.2816

351082,2.4504931724\H,-1.2587066695,-1.8975430254,3.5754854481\O,-1.22
14741832,-1.8379256761,-0.8698912008\C,-2.3438645748,-2.453610028,-0.8
426263179\O,-3.4282688536,-2.1063101861,-0.2709647414\H,-2.3692463782,
-3.4141394636,-1.3892220735\O,-1.754854202,0.936697735,-1.5848723462\C
,-3.0207669097,1.0463225838,-1.7477314161\O,-3.9573511251,0.6425647957
,-0.9838593167\H,-3.3350228861,1.5592668838,-2.6750212089\C,1.44295040
61,1.6096180942,-0.4879370429\C,2.8610345589,1.6235953152,-0.230147590
5\C,0.7526093331,2.8038465556,-0.7700266673\C,3.2834351283,0.257076621
2,-0.080350616\C,3.5565295629,2.8471444212,-0.2472635791\C,1.471051843
1,4.0133905194,-0.7797861593\H,-0.3102323549,2.7799912812,-1.003217167
8\C,2.851990064,4.0362336864,-0.5193241949\H,4.6363522869,2.8770575833
,-0.0881845648\H,0.946340571,4.9455770485,-1.0060427248\H,3.3931150504
,4.9862312409,-0.543254946\N,0.9366075725,0.3228962264,-0.4428401864\C
,4.5607960435,-0.2006500108,0.4153879215\C,5.3230590424,0.6078389959,1
.3132661935\C,5.1184850124,-1.4634759693,0.0549739613\C,6.5650157536,0
.1899749617,1.794068026\H,4.898149178,1.5483967998,1.669832001\C,6.363
8482736,-1.8726993055,0.5363787731\H,4.5800916302,-2.1123763295,-0.637
093831\C,7.1012121942,-1.050277552,1.4053420972\H,7.1148723111,0.82969
61624,2.4907331928\H,6.7670255666,-2.8413310893,0.2264089683\H,8.07528
92217,-1.3748044632,1.7810719339\C,2.1162383952,-0.6139100993,-0.56370
74505\C,2.2935000658,-0.9818683879,-2.0997411219\C,1.9039235865,-1.990
6074375,0.1389099482\C,1.6432201433,-2.3618400477,-2.2708328161\H,3.37
39367177,-1.0342420808,-2.3192514567\H,1.8664170774,-0.1964490331,-2.7
417921166\C,1.9788248029,-3.0882301617,-0.952867586\H,0.9190556477,-1.
9898747543,0.6187312415\H,2.6442185871,-2.1407047057,0.9393824707\H,0.
5531360263,-2.2529982209,-2.3694487596\H,2.0175661725,-2.8921708425,-3
.162741587\H,1.2934669335,-3.9251601167,-0.7420454778\H,2.9955327821,-
3.5180468382,-1.0070491403\\Version=EM64L-G09RevA.01\State=3-A\HF=-172
8.8298395\S2=2.010762\S2-1=0.\S2A=2.000072\RMSD=9.221e-09\RMSF=8.154e-
06\Dipole=1.3739728,0.1830226,-0.2745126\Quadrupole=-6.0375204,8.05445
89,-2.0169385,-2.687216,5.9929202,1.2087948\PG=C01 [X(C22H21N1O8Rh2)]\
\@

TS5

1\1\GINC-SHI_03\FTS\UBPW91\GenECP\C22H21N1O8Rh2(3)\YIN\26-Dec-2014\0\\
#p opt=(calcfc,ts,noeigen) genecp bpw91\\Title Card Required\\0,3\Rh,-
1.1889140714,-0.0257801688,-0.4659497784\Rh,-3.5351860331,-0.352185857
1,-1.074952079\O,-1.8684056991,1.1958827349,1.0655688527\C,-3.13147314
19,1.377825211,1.176801366\O,-4.0692402908,0.9011328567,0.4575877246\H
,-3.4422097972,2.036571629,2.0081753795\O,-1.4106715713,-1.6487656444,
0.8004146825\C,-2.5509577492,-2.2289820957,0.8518981355\O,-3.615523055
3,-1.9458282184,0.2111578507\H,-2.6146689424,-3.08757995,1.5449287052\
O,-0.7293728271,-1.2777088684,-2.0558139552\C,-1.691314198,-1.77419209
97,-2.7396656781\O,-2.9446941515,-1.6025777635,-2.5874294043\H,-1.3881
737487,-2.4377548401,-3.5699635682\O,-1.1873569214,1.5689544995,-1.783
6812428\C,-2.2673613963,1.8388081569,-2.4143641088\O,-3.3972311922,1.2

503576969,-2.3451701053\H,-2.2070179851,2.6968451335,-3.1082103618\C,1
.3633268623,1.6319675865,0.0413239036\C,2.7823558234,1.6096303193,-0.1
374680125\C,0.6867118542,2.839164074,0.2403181676\C,3.1548476886,0.224
4140117,-0.2789776205\C,3.5071579075,2.8110391006,-0.17649747\C,1.4352
672004,4.0392140326,0.2314118326\H,-0.3885940914,2.8538319632,0.407884
1274\C,2.8200240237,4.0282709706,0.0158257005\H,4.5849267291,2.8048195
005,-0.3597068958\H,0.9173522951,4.9892134358,0.3889619978\H,3.3759927
245,4.9696752707,-0.003927908\N,0.8495759903,0.3223956564,-0.013807155
2\C,4.5159771614,-0.263520034,-0.5337133458\C,5.5963855728,0.191333144
2,0.2657028349\C,4.8115547438,-1.1508985976,-1.5999830602\C,6.90571077
24,-0.2425320471,0.0254916806\H,5.3923820032,0.8700505323,1.0981106646
\C,6.1231943664,-1.5766945662,-1.8414615123\H,4.0093153838,-1.46781822
21,-2.2711503185\C,7.176266551,-1.1307586707,-1.0272929935\H,7.7181919
501,0.1118365418,0.6666770095\H,6.3252338571,-2.2510871137,-2.67874359
63\H,8.1996328025,-1.4664575425,-1.2165009263\C,1.9457591212,-0.552051
8637,-0.0305804916\C,1.8190862528,-2.0401795486,-0.3168120222\C,2.1906
794867,-0.8980402897,2.2104953661\C,1.5667239355,-2.8997353846,0.94199
36874\H,2.7709681474,-2.368031285,-0.7621654801\H,1.0352023563,-2.2047
637722,-1.0695910983\C,2.4573980322,-2.36341813,2.0792625818\H,1.18851
92726,-0.585116292,2.5200202794\H,2.996027671,-0.2069149917,2.47378940
22\H,0.5109778802,-2.8124935233,1.2395468339\H,1.768882413,-3.96389865
12,0.7261468931\H,2.2329963309,-2.9085678149,3.0199386518\H,3.52301470
01,-2.5449792116,1.8521638773\\Version=EM64L-G09RevA.01\State=3-A\HF=-
1728.7976883\S2=2.01808\S2-1=0.\S2A=2.00015\RMSD=5.410e-09\RMSF=1.297e
-05\Dipole=1.396884,-0.0445104,0.2669631\Quadrupole=-3.7980015,5.48205
19,-1.6840504,-3.5032675,-3.6116314,2.1731611\PG=C01 [X(C22H21N1O8Rh2)
]\\@

C3

1\1\GINC-SHI_02\FOpt\UBPW91\GenECP\C22H21N1O8Rh2(3)\YIN\24-Dec-2014\0\
\#p opt genecp bpw91\\Title Card Required\\0,3\Rh,-0.2833185298,0.3684
663496,0.1595895\Rh,-0.7436753402,0.9557943134,2.4841443864\O,1.673433
9767,0.0073815347,0.7408937313\C,1.9778883499,0.2021210768,1.969591582
9\O,1.228109804,0.5970136963,2.9219742325\H,3.0319668579,-0.000804623,
2.2332117019\O,-0.7545474383,-1.5857094358,0.6712950037\C,-1.087227308
6,-1.8266804017,1.8841601753\O,-1.1800708265,-1.0109157354,2.859383888
5\H,-1.3237060449,-2.8824087928,2.1100183844\O,-2.2764930797,0.7809382
895,-0.2270925511\C,-3.0191776519,1.1401619653,0.7513450052\O,-2.70244
30803,1.2926724223,1.9770425012\H,-4.0747915013,1.3435921467,0.4940376
621\O,0.1491301237,2.3680002796,-0.1449315948\C,0.0417906802,3.1700159
476,0.8462168267\O,-0.2957947397,2.9079685994,2.0481255005\H,0.2749681
405,4.227539172,0.625707742\C,1.1364874744,0.5982440826,-2.6024010901\
C,0.9236022859,0.4439627432,-4.0046603408\C,2.2590816438,1.2666991352,
-2.1144139994\C,-0.3121497081,-0.2909596209,-4.1451189968\C,1.82324657
56,1.0162831359,-4.9216253159\C,3.1727373808,1.8052228543,-3.048263551
8\H,2.4309185936,1.3640763307,-1.0439264159\C,2.9551493308,1.691916776

3,-4.4305116501\H,1.6438738466,0.9463697383,-5.9976421334\H,4.0609330595,2.3267514535,-2.6808608561\H,3.6686974819,2.1322644895,-5.1321198542\N,0.0762306007,-0.0142761016,-1.8917852778\C,-0.9514856902,-0.6490627732,-5.4139425022\C,-0.1780816403,-1.1543603467,-6.4910927079\C,-2.3415715888,-0.4640322479,-5.6246585756\C,-0.7719327927,-1.4690265797,-7.7185509521\H,0.8898023168,-1.3313379623,-6.3409369148\C,-2.9296586084,-0.7708299489,-6.8563361828\H,-2.9519771381,-0.0373575898,-4.8255707225\C,-2.1497366265,-1.2772898504,-7.9087349163\H,-0.1572546792,-1.8709278027,-8.5291638563\H,-4.0014336625,-0.6053573014,-6.9988919671\H,-2.6121820237,-1.5192809591,-8.8696182891\C,-0.7634982005,-0.5724919439,-2.8075871805\C,-1.9453667871,-1.4210626405,-2.4183503674\C,0.5821487356,-3.436030974,-2.638517138\C,-1.9098247822,-2.8822547929,-2.9353808972\H,-2.8730962561,-0.9486153791,-2.7861361631\H,-2.0234506923,-1.4327069626,-1.3237886177\C,-0.8252009696,-3.7768193039,-2.2735399577\H,1.2927452508,-3.057709817,-1.9025613063\H,0.9193131285,-3.521700381,-3.6751450367\H,-2.9011148773,-3.3277818597,-2.7312995451\H,-1.7814364333,-2.8972195339,-4.0305675286\H,-0.9509383731,-3.735859187,-1.1785269334\H,-1.0496915377,-4.8210008956,-2.5796476399\\Version=EM64L-G09RevA.01\State=3-A\HF=-1728.8095782\S2=2.00965\S2-1=0.\S2A=2.000059\RMSD=4.339e-09\RMSF=7.473e-06\Dipole=-0.1199136,-0.3047793,-1.6062169\Quadrupole=5.6596265,-3.8254661,-1.8341604,4.9700978,4.587544,-0.7059612\PG=C01 [X(C22H21N1O8Rh2)]\\@

D3

1\1\GINC-SHI_02\FOpt\RBPW91\GenECP\C22H21N1O8Rh2\YIN\16-Dec-2014\0\\#p opt bpw91/genecp\\Title Card Required\\0,1\Rh,0.0405073235,0.0301682545,0.0361977209\Rh,0.3492048765,-0.0797833661,2.4652943502\O,2.1005205351,-0.0862635209,-0.1323758921\C,2.7856513293,-0.166938294,0.94663365\O,2.3755196105,-0.1772396926,2.1539716068\H,3.8804633343,-0.2354436361,0.8065073795\O,-0.0405739724,-2.0441262702,0.0892634482\C,0.0807038885,-2.6381224857,1.2169547837\O,0.2499586259,-2.1260840485,2.3707875799\H,0.0312435152,-3.7421967827,1.1785821291\O,-1.9977215253,0.1339911071,0.4222728922\C,-2.3876857558,0.1048383856,1.6415436344\O,-1.6865331319,0.0136264703,2.7023310812\H,-3.4819574831,0.1674561974,1.7895880941\O,0.1206455262,2.0925274139,0.223684846\C,0.290015683,2.5818594751,1.3947471045\O,0.4318148873,1.9679526503,2.5030123777\H,0.3165966778,3.6862687957,1.4457106114\C,0.6344999243,1.0011056203,-2.8883303095\C,0.3387163562,0.8779576471,-4.3235599926\C,1.6463294396,1.9347152752,-2.4663232644\C,-0.6590851053,-0.070937183,-4.4615177945\C,1.0349688084,1.6913740793,-5.2823311924\C,2.2936149116,2.6785122647,-3.4249508933\H,1.878351653,2.041452762,-1.4096992863\C,1.9901689176,2.569594812,-4.8325375272\H,0.784780956,1.6157039247,-6.3433071721\H,3.0631470159,3.3918719096,-3.1148042499\H,2.5272309815,3.2080038508,-5.5392731317\N,-0.1093907384,0.1818720883,-2.1458324928\C,-1.1209102178,-0.6340343894,-5.7438365631\C,-0.1459619761,-1.0290963874,-6.6970152124\C,-2.4840002974,-0.8114624557,-6.0862450784\C,-0.5163460872,-1.5772441186,-7.9306716671

\H,0.9120232085,-0.9303066808,-6.4413216768\C,-2.851318124,-1.3510710822,-7.3254746366\H,-3.2662318628,-0.4999472257,-5.3927985393\C,-1.8721137642,-1.7395224004,-8.2524033444\H,0.2581595978,-1.8862201646,-8.6385251274\H,-3.9115473766,-1.4662797102,-7.5680290103\H,-2.1636191031,-2.167812879,-9.2153467034\C,-1.0097343556,-0.5662585628,-3.063260867\C,-2.5266942678,-0.3709981222,-2.648582111\C,-0.778336932,-2.1264506294,-2.9797603652\C,-3.0715603911,-1.7793904127,-2.3139694024\H,-3.0861908786,0.0950146425,-3.4720368171\H,-2.5866810299,0.3099138666,-1.7912837592\C,-2.1807874848,-2.7471876411,-3.1097502426\H,-0.3585241812,-2.349294213,-1.9917195066\H,-0.0679021717,-2.4759094086,-3.7448989847\H,-2.9525311012,-1.9650397789,-1.2341118601\H,-4.1436689043,-1.8780460655,-2.5529074931\H,-2.2049492887,-3.7788240774,-2.7198846613\H,-2.4964132849,-2.786724025,-4.1660097428\\Version=EM64L-G09RevA.01\State=1-A\HF=-1728.8655281\RMSD=7.110e-09\RMSF=1.635e-05\Dipole=-0.3472019,-0.1162911,-2.5324785\Quadrupole=4.0106081,-0.1063111,-3.904297,5.3712557,-0.8518937,2.7823285\PG=C01 [X(C22H21N1O8Rh2)]\\@

TS6

1\1\GINC-SHI_03\FTS\RBPW91\GenECP\C22H21N1O8Rh2\YIN\27-Dec-2014\0\\#p opt=(calcfc,ts,noeigen) genecp bpw91\\Title Card Required\\0,1\Rh,-1.2324320708,0.1153285518,0.1111493398\Rh,-3.6316891747,-0.1619501824,0.5191956241\O,-1.267558192,1.6316169611,1.5214880438\C,-2.3900948756,1.9115066374,2.0702148934\O,-3.5320136735,1.3799790528,1.8708657981\H,-2.3601969135,2.7266610356,2.8172534317\O,-0.9194220074,-1.2315360411,1.6606293187\C,-1.9486607287,-1.7100955276,2.2563291654\O,-3.1796899694,-1.4835891998,2.026560218\H,-1.7333844877,-2.4159857148,3.0807205832\O,-1.3947636114,-1.4335629196,-1.2649137315\C,-2.545118646,-1.9735843528,-1.426372645\O,-3.6466824753,-1.6955763572,-0.8481537192\H,-2.5832572899,-2.7916322298,-2.1700400512\O,-1.7431252758,1.4369537518,-1.3976423148\C,-2.9871530018,1.6543433946,-1.6065035034\O,-3.9975925543,1.1690241616,-0.9978992687\H,-3.2114963287,2.3601210344,-2.4279842032\C,1.4978197043,1.6794867314,-0.1963786242\C,2.931903262,1.5882215022,-0.12342806\C,0.8827248725,2.9544116372,-0.2769512916\C,3.2436590125,0.1947713423,-0.1050544809\C,3.7428141696,2.7497592873,-0.1517593856\C,1.7004167048,4.0791722669,-0.2949409443\H,-0.2003857694,3.0387918197,-0.3414178071\C,3.1198451671,3.9879142897,-0.2349708746\H,4.832721708,2.6658175195,-0.1294257777\H,1.2385312804,5.0683890318,-0.3684520097\H,3.7194801706,4.9015491485,-0.265928056\N,0.9124798697,0.4311939537,-0.1958518456\C,4.6023377041,-0.3613841462,-0.3083332147\C,5.6543418773,-0.0162303963,0.5720267498\C,4.9024973899,-1.177292461,-1.4225555028\C,6.9544387095,-0.4936325427,0.3616947349\H,5.4476959112,0.6266264712,1.4325324889\C,6.2053148019,-1.6477472741,-1.6352525474\H,4.1194132297,-1.4122999262,-2.1470144189\C,7.2336783063,-1.3157078055,-0.7405695642\H,7.7506627076,-0.2210502744,1.0601404837\H,6.417414464,-2.2717861847,-2.5078469533\H,8.248220084,-1.6887284844,-0.905260618\C,1.9361884296,-0.4967276334,-0.1093091385\C,1.7047467604,-1.9694208476,-0.4087880047\C,2.58

46561321,-0.6459777225,1.7460171054\C,1.7975095553,-2.8198521392,0.884
6254691\H,2.4673013287,-2.3109330736,-1.1255160257\H,0.7236449116,-2.0
744989025,-0.8898738031\C,2.8323317676,-2.1374706238,1.7870473141\H,1.
6123223373,-0.3179212073,2.131953259\H,3.3892606217,-0.0349337658,2.16
96290363\H,0.8168648975,-2.8175912023,1.3815002669\H,2.0646638545,-3.8
652570014,0.6599868946\H,2.7533628878,-2.4815967838,2.8361745066\H,3.8
616164551,-2.3568436587,1.4564216599\\Version=EM64L-G09RevA.01\State=1
-A\HF=-1728.8395591\RMSD=6.003e-09\RMSF=1.436e-05\Dipole=3.1486596,-0.
5070779,0.2941402\Quadrupole=-1.1580126,3.3379853,-2.1799727,-6.586690
2,4.1080852,1.6836877\PG=C01 [X(C22H21N1O8Rh2)]\\@

E3

1\1\GINC-SHI_02\FOpt\RBPW91\GenECP\C22H21N1O8Rh2\YIN\24-Dec-2014\0\\#p
 opt genecp bpw91\\Title Card Required\\0,1\Rh,-0.2686691636,0.1698998
519,-0.1596050484\Rh,-0.707360369,0.07318038,2.2410198625\O,1.74717231
8,0.0294662779,0.2973535185\C,2.072580282,-0.0629686116,1.5326024318\O
,1.3172475569,-0.0677740265,2.55984526\H,3.157382574,-0.1490197163,1.7
295134773\O,-0.3548308871,-1.9030413991,-0.160702232\C,-0.5941979853,-
2.491065134,0.9522305179\O,-0.7995835395,-1.9750643623,2.0989691508\H,
-0.6265097999,-3.5956451422,0.9059786455\O,-2.3194959543,0.3031226118,
-0.4388403876\C,-3.0610655969,0.3063504485,0.6057592584\O,-2.715735310
4,0.2210897865,1.8295820501\H,-4.1468201778,0.3940350363,0.4144573045\
O,-0.2142241041,2.2327726139,0.0313828642\C,-0.3887626766,2.7284264754
,1.1992774453\O,-0.5957476983,2.1217944711,2.3014029147\H,-0.353301333
4,3.8323647389,1.2536744799\C,1.071162671,1.1074265315,-2.9115598253\C
,1.0498547653,0.9504399784,-4.313556316\C,1.97203812,1.9766093886,-2.2
873358703\C,-0.0224223255,-0.0702320796,-4.6481800889\C,1.9219584503,1
.6784394948,-5.1233795226\C,2.8536739658,2.6995818168,-3.1086721269\H,
1.9838847414,2.0849156972,-1.2042898642\C,2.8312773449,2.5573455178,-4
.5070276368\H,1.8953515269,1.5774638696,-6.2122141327\H,3.5669886261,3
.3887037218,-2.6480529167\H,3.5242582631,3.1375611717,-5.1226094194\N,
0.0835160307,0.2682819399,-2.2940608422\C,-1.1055574089,0.5211304723,-
5.5698810645\C,-1.19061385,0.2036908693,-6.9387083371\C,-2.0166646151,
1.4632732664,-5.045586045\C,-2.1621179984,0.8019169312,-7.7574897311\H
,-0.5003651735,-0.5168469628,-7.383616651\C,-2.9879875707,2.0581108844
,-5.8604844495\H,-1.961328528,1.736740298,-3.9872869351\C,-3.066629811
5,1.7281082268,-7.2225237308\H,-2.2095273083,0.5360740032,-8.817552766
\H,-3.6847093515,2.7821475101,-5.428453844\H,-3.8261777367,2.189475853
9,-7.8597257087\C,-0.5528557273,-0.3786804192,-3.2434409825\C,-1.56638
93658,-1.4606969999,-3.0790502363\C,0.587044026,-1.4250144168,-5.14752
48331\C,-0.9849606463,-2.7785348743,-3.6685339109\H,-2.4715457317,-1.1
838951087,-3.6506950345\H,-1.8450837426,-1.5861384721,-2.0269001172\C,
-0.4354869333,-2.5762791783,-5.0917031009\H,1.4450672695,-1.6608594772
,-4.4930979835\H,1.0025509783,-1.2971730366,-6.1609786773\H,-0.1796222
153,-3.132173943,-3.0011968824\H,-1.7726263416,-3.5510303537,-3.663510
8425\H,0.0473934426,-3.5051464003,-5.4428483715\H,-1.2691720065,-2.369

2575249,-5.7857854574\\Version=EM64L-G09RevA.01\State=1-A\HF=-1728.899
0131\RMSD=6.882e-09\RMSF=1.162e-05\Dipole=0.0846065,-0.2592621,-2.5291
357\Quadrupole=2.3899573,2.8459014,-5.2358587,1.2198244,3.5113408,3.52
60685\PG=C01 [X(C22H21N1O8Rh2)]\\@

Reference

[1] Yan, Y.; Wang, Z. *Chem. Commun.* **2011**, *47*, 9513–9515.

[2] (a) Stafford, J. A.; McMurry, J. E. *Tetrahedron Lett.* **1988**, *29*, 2531–2534; (b) Utimoto, K.; Tamura, M.; Sisido, K. *Tetrahedron* **1973**, *29*, 1169–1171.

[3] (a) Chen, K.; Zhang, Z.; Wei, Y.; Shi, M. *Chem. Commun.* **2012**, *48*, 7696–7698; (b) Chen, K.; Sun, R.; Xu, Q.; Wei, Y.; Shi, M. *Org. Biomol. Chem.* **2013**, *11*, 3949–3953.

[4] Guo, F.; Wang, L.; Wang, P.; Yu, J.; Han, J. *Asian J. Org. Chem.* **2012**, *1*, 218–221.

[5] Zhang, X.; Ke, Z.; DeYonker, N. J.; Xu, H.; Li, Z.; Xu, X.; Zhang, X.; Su, C.-Y.; Phillips, D. L.; Zhao, C. *J. Org. Chem.* **2013**, *78*, 12460–12468.